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A COMPLETE COURSE *of* VOLUMETRIC ANALYSIS

W. T. BOONE

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A Complete Course of Volumetric Analysis

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A Complete Course of Volumetric Analysis

FOR MIDDLE AND HIGHER
FORMS OF SCHOOLS

BY

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PREFACE

This course of exercises is intended to provide a thorough grounding in the principles and practice of Volumetric Analysis. The analytical methods introduced are modern and reliable, and there is considerable variety in their application. The theory underlying the various processes is fully dealt with, while the plan of the Course is designed to secure exact knowledge and sound mental training. That volumetric analysis can be made an instrument of great educational value is generally acknowledged. It demands thoughtful grasp of the problems presented, and clear and logical reasoning; it affords scope for the exercise of imagination, ingenuity, and judgment; it quickens the senses, increases manipulative skill, and trains hand and eye to work in harmony; it encourages neatness, precision, and accuracy; and, under the guidance of a stimulating teacher, it may whet the appetite for research.

The present course as a whole is progressive, and assumes no previous knowledge of analysis. The different volumetric methods introduced are dealt with in separate chapters, in which the exercises are usually grouped according to their difficulty. For beginners, the best results will probably follow from taking the work in the order suggested in the book, reserving the more difficult portions until a general acquaintance with the chief methods has been obtained. It may be found convenient, for instance, to make a break at Exercise 42 in the work on acidimetry and alkalimetry (Chapter VI). Although here and there the solution of a problem depends upon a result previously obtained, the bulk of the exercises can be worked quite independently of one another, and selections can easily be made to meet individual requirements. As simple estimations of most bases and of the commoner acids have been included in the course, it will be found useful to the general student and to those preparing for natural science scholarships to the Universities, and for Preliminary, Intermediate, and other examinations up to the standard usually demanded for a "pass" Degree.

For carrying out the earlier exercises, full directions are given; afterwards, only those are introduced which are necessary to meet the peculiar difficulties of each problem, secure orderly and accurate work, and economize time. The questions which have been included should not be ignored, as they focus attention upon some important theoretical consideration or lead up to a subsequent exercise.

Chapter X contains miscellaneous exercises based on work done previously. Chapter XI, though wholly theoretical, has been inserted to provide a simple explanation of solution and of the behaviour of indicators from the ionic standpoint.

Amongst the works which have been consulted during the compilation of the course, and to which the writer feels indebted, are:—

Sutton's *Volumetric Analysis.*
Schimpf's *Volumetric Analysis.*
Clowes and Coleman's *Quantitative Analysis.*
Ostwald's *Foundations of Analytical Chemistry.*
Walker's *Introduction to Physical Chemistry.*
Journal of the Chemical Society.
Chemical News.

WILLIAM T. BOONE.

CHELTENHAM,
January, 1918.

CONTENTS

Chap. | Page

I. Introduction - - - - - - - - 1

II. Simple Apparatus for measuring Liquids - - 5

III. Methods of ascertaining when Reactions are complete. End-points - - - - - 14

IV. Common Indicators - - - - - - - 18

V. Standard or Volumetric Solutions - - - 25

VI. Acidimetry and Alkalimetry - - - - - 35
- Direct Method - - - - - - - - 36
- Backward Titration Method - - - - - 54
- Use of Two Indicators in one Estimation - - 58
- Estimation of Ammonium Salts - - - - 62
- Estimation of Organic Acids and of their Molecular Weights - - - - - - - - 67

VII. Methods depending on Direct Oxidation and Reduction - - - - - - - - 72
- Use of Potassium Permanganate - - - - 72
- Use of Potassium Dichromate - - - - 86

VIII. Methods involving Indirect Oxidation. Iodometry - - - - - - - - - 90

IX. Methods involving Precipitation - - - - 107
- Use of Silver Nitrate - - - - - - 107
- Use of Potassium Thiocyanate - - - - 114
- Use of Sodium Sulphide - - - - - - 116
- Use of Potassium Cyanide - - - - - 120
- Use of Uranyl Acetate - - - - - - 122

Chap. Page
X. Miscellaneous Exercises - 125
XI. Notes on Electrolytic Dissociation and Indicators - 134
Indicators used in Acidimetry and Alkalimetry - 137
Some other Indicators - 142
Table of Standard Solutions in Common Use - 145
Table of Atomic Weights - 150
Notes on the Exercises - 151
Answers to Questions - 153
Index - 160

VOLUMETRIC ANALYSIS

CHAPTER I

Introduction

The fundamental laws of Chemistry, and the composition of the innumerable substances now known to us, have been established by gravimetric methods. These are necessarily slow, are often laborious, and may demand considerable manipulative skill in separating and purifying the various products. But the great store of knowledge thus accumulated has made possible other methods of quantitative analysis involving no separation, in which the comparatively quick operation of measuring volumes largely replaces that of weighing. These are known as "volumetric"; and, besides being shorter than gravimetric methods, are at least as accurate. To show how such estimations become possible, let us consider the problem of determining the weight of hydrogen sulphate (H_2SO_4) in a given volume of dilute sulphuric acid. When determined gravimetrically, the acid is precipitated as barium sulphate; the precipitate is treated so as to make it granular, collected on a filter, washed, and dried; the filter is burned; the reduced sulphate contained in the ash is reoxidized; and, lastly, the whole is carefully ignited until constant weight is obtained. By such means it has been ascertained that 137 parts by weight of barium, contained in one of its soluble salts, are just sufficient to react with 98 parts of sulphuric acid; also, that anhydrous barium chloride contains $\frac{137}{208}$ of its weight of the metal. Now, if a definite weight of this salt is dissolved up to a known volume, the weight contained in 1 cu. cm. of the solution is known. Such a solution is said to be of "known strength"; and if the volume necessary to complete the precipitation of the acid can be ascertained, the weight of barium chloride used can be calculated, and the problem solved by making use of the fact expressed in the equation—

$$\underbrace{H_2SO_4}_{98} + \underbrace{BaCl_2}_{208} = BaSO_4 + 2\,HCl,$$

that the required weight of hydrogen sulphate is $\frac{98}{208}$ times that of the barium chloride. In practice, however, this method fails on account of the turbidity produced; for the "end-point", or point when precipitation is complete, is obscured, and the exact quantity of barium chloride necessary to react with the acid is not readily ascertained. The difficulty can be overcome by substituting a solution of caustic soda of known strength for that of the barium salt; for no precipitate results from its reaction with the sulphuric acid, and the introduction of a few drops of litmus solution will at once show when neutralization of the acid has been accomplished. To arrive at this condition, acid and alkali have been mixed in the proportion of 98 : 80, as expressed by the equation—

$$\underbrace{H_2SO_4}_{98} + \underbrace{2\,NaOH}_{80} = Na_2SO_4 + 2\,H_2O,$$

and the weight of acid originally present is $\frac{98}{80}$ that of the NaOH used. On account of its use in such a determination, litmus is called an "indicator". Since caustic soda is deliquescent, and the composition of any particular sample is known only roughly, a solution of "known strength" cannot be made by simply dissolving up a weighed quantity to some definite volume. Its "strength" is only roughly known, and must be ascertained with exactness by a special determination. This drawback is minimized by preparing a large quantity, ascertaining its exact "strength" once for all, when it may be used for a large number of determinations like that required by our problem.

Speaking generally, volumetric methods are dependent upon our ability to recognize the completion of some reaction in which the substance to be analysed takes part. Good results may be obtained by them if the following conditions are fulfilled:—

1. The solutions prepared must be homogeneous.
2. The "strength" of one of the solutions used in an estimation must be accurately known. The "strength of a solution" is the concentration of its solute, or weight of dissolved substance in 1 cu. cm. [This must not be confounded with the term "strength of acid", &c., when referred to from the dissociation standpoint.]
3. Accurate measurements of the volumes of solutions used must be possible.
4. The point at which just sufficient of one solution has been added to another to complete some particular reaction must be easily detected. This is the "end-point" of the reaction.

The first condition can be secured by thorough mixing. The "strength of a solution" may be determined in various ways. A definite weight of solid of known composition may be dissolved up to a given volume. If the exact composition of the weighed substance is unknown, the strength of the solution made must be ascertained by finding the volume necessary to react with a definite volume of some other solution whose strength is known, and then making use of the equation expressing the reaction. Another way of determining the strength is to make use of a gravimetric method; as, for example, in estimating sulphuric acid by precipitating it as barium sulphate and weighing the latter.

The "strength of a solution" is usually given as the weight of solute in grammes per cubic centimetre. If 58.46 grm. of pure sodium chloride are dissolved up to 1 l., each cubic centimetre will contain 0.05846 grm. of the salt; and the strength of the solution will be given

$$1 \text{ cu. cm.} = 0.05846 \text{ grm. NaCl};$$

or, for reactions in which chlorides take part,

$$1 \text{ cu. cm.} = 0.03546 \text{ grm. Cl}.$$

You will note that in such statements = means "contains" or "yields up". In some cases it may mean "reacts with".

Before proceeding to the analytical processes, we will first examine the apparatus commonly used for the measurement of small quantities of liquid and test the accuracy of their graduation. We will then get acquainted with the chief methods of determining the end-points of certain reactions.

CHAPTER II

Simple Apparatus for measuring Liquids

In European laboratories the graduation of measuring vessels is usually based upon the cubic centimetre as unit—that volume occupied by 1 grm. of pure water at 4° C. It follows that "x" cu. cm. of water measured at ordinary temperatures really weigh something under "x" grm.

Note.—In the following exercises degrees of temperature will be expressed according to the Centigrade scale unless otherwise specified.

One litre of water should weigh—

At 10°: 998.4 grm., losing on an average 0.1 grm. for each degree up to 14°.
At 15°: 997.8 grm.
At 16°: 997.7 grm., losing 0.2 grm. for each degree up to 20°.

This does not interfere with the accuracy of volumetric methods, as practically all measurements are made within a degree or two of 15°, and all vessels are graduated to the same standard.

In America the unit of volume adopted is that of 1 grm. of water at 15°, which is, of course, slightly in excess of 1 cu. cm.

The simplicity of the system enables us to read quantities of water, and even of dilute solutions, such as are used in ordinary volumetric work, either as grammes or cubic centimetres.

Exercise 1.—Examine the vessels commonly used for measuring liquids in the laboratory.

(i) *Cylindrical graduated glass jars* used for rough measurements. The divisions show cubic centimetres or multiples of cubic centimetres, and are often numbered in both directions for convenience in reading. (See fig. 1.)

(ii) *Narrow-necked flasks* (fig. 2), whose capacities up

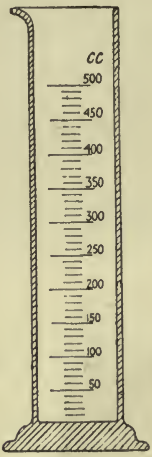

Fig. 1

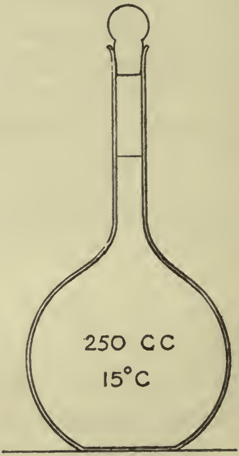

Fig. 2

to the etched line are given at the stated temperature. These vessels *do not deliver* the quantities shown, as the liquid clinging to the flask is not allowed for. Flasks which deliver the quantity indicated are marked with A (ausguss) or D (deliver). The better sorts are provided with glass stoppers, and some have graduation marks on the stem. A quarter-litre flask at 15° should hold 249.5 grm. of pure water.

Litre, half-litre, and quarter-litre flasks are in commonest use.

(iii) *Pipettes.*—The commonest form is that of a long narrow tube tapering to a fine nozzle at its lower end and having a cylindrical bulb near the middle. It is important to note that the nozzle is unbroken. When filled with liquid to the mark, a pipette should *deliver* the quantity indicated on the bulb when allowed to drain for a few seconds. More or less always remains in the nozzle, and the quantity to be left is best determined by experiment. Some pipettes resemble small burettes, and are graduated to deliver any volume up to 10 cu. cm. or more.

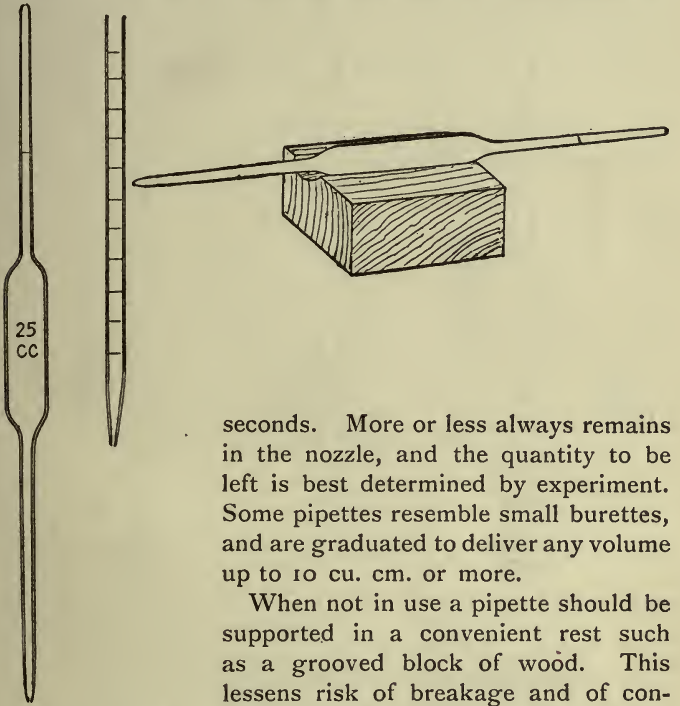

Fig. 3.—Pipettes

When not in use a pipette should be supported in a convenient rest such as a grooved block of wood. This lessens risk of breakage and of contamination by material spilt on the bench. (Fig. 3.)

(iv) *Burettes* are long narrow tubes commonly made to deliver any required volume of liquid up to 50 cu. cm. They are graduated into fifths or tenths of a cubic centimetre throughout the greater part of their length, and read downwards. In Mohr's burette the liquid is generally allowed to fall out through a rubber tube provided with nozzle and pinchcock. Sometimes the tube is merely plugged with a piece of glass rod. On carefully pinching the rubber, the liquid drops out as required. Burettes fitted with glass taps are necessary when working with standardized potassium permanganate or other solution decomposed by rubber. As a rule, liquids can be more accurately measured out from burettes than pipettes. The usual method of suspending burettes when in use is shown in fig. 4.

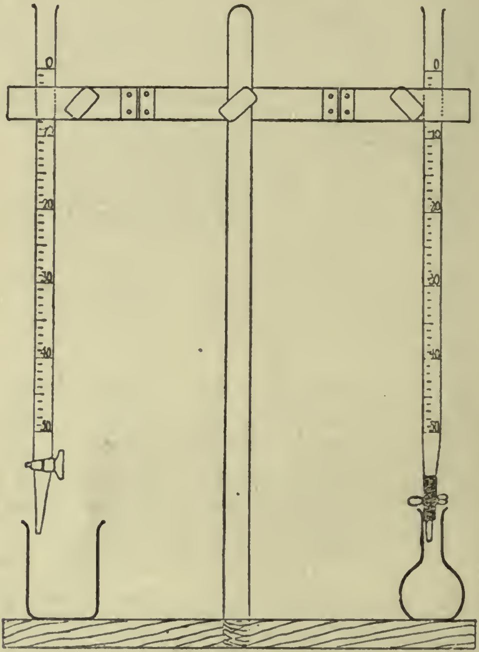

Fig. 4

Floats, though not recommended for general use, lessen a beginner's chance of error in reading volumes delivered from burettes. The simplest form consists of a glass tube with a line etched round it (to which the readings are made) and weighted with mercury at one end, to cause it to float vertically in liquids of about the density of water. They should slide easily into the burette and not tilt to one side.

A simple float may be made by dropping a small globule of mercury into a test-tube of suitable diameter, and drawing the tube off to a point about two inches from the rounded end. Into this end a small piece of platinum wire may be fused and looped for convenience of withdrawal. Readings may be made to a mark scratched upon the glass or to the end of the looped wire. Fig. 5 shows this and other common forms.

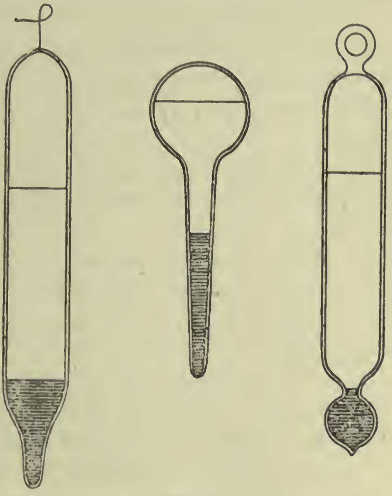

Fig. 5

Exercise 2.—Calibrate some flasks, or test the graduated flasks supplied.

Directions.—1. Choose flasks preferably with long narrow necks. Why? Of ordinary round flasks with flat bottoms those about—

4¾	in., or	12	cm.,	diameter	hold	1	l.
3¾	,,	9½	,,	,,	,,	½	,,
3¼	,,	8	,,	,,	,,	¼	,,
3	,,	7½	,,	,,	,,	200	cu. cm.
2¼	,,	5½	,,	,,	,,	100	,,

2. Roughly test their capacity by pouring in the required

volume of water. If this reaches about half-way up the neck the flasks will do.

3. Cleanse with distilled water and dry thoroughly inside and out.

To dry a flask inside warm it over a Bunsen flame while passing a current of air from a bellows through a glass tube reaching to the bottom of the flask. The air may be filtered from dust by loosely plugging the tube with cotton-wool.

4. Carefully counterpoise the flask on a balance: one used for rougher weighings will do so long as it is accurate within 0.1 grm.

5. Weigh into it the proper quantity of distilled water calculated from the data previously given. For instance, at 15°, 997.8 grm., 498.9 grm., and 249.5 grm. should be weighed out for a litre, half-litre, and quarter-litre respectively. A small excess is best withdrawn by a rolled-up filter-paper. Drops spilled on the flask or balance pan must be removed before the final weighing.

6. When the water inside the neck has drained down, make a neat horizontal scratch exactly level with the lowest part of the meniscus or curved surface of the liquid. This will be in a convenient position if care has been taken in selecting the flask.

7. Scratch—or, better, *etch*—the capacity and temperature on the bulb, thus:—

$$\left[\begin{matrix}\text{250 cu. cm.}\\ 15^{\circ}\text{ C.}\end{matrix}\right]$$

To etch the Figures.—Smear lightly and evenly one side of the bulb with melted paraffin, and, when dry, neatly scratch the figures through the wax with a metallic point so as to lay the glass bare. Mix up some calcium fluoride and strong sulphuric acid in a leaden dish placed in a fume closet, and warm gently till fumes of hydrogen fluoride appear; then hold the waxed surface down upon the dish for one minute, taking care that the wax does not melt.

The figures should show up distinctly on removing the wax.

Exercise 3.—Test the accuracy of your pipettes by finding the weight of distilled water delivered by the instruments.

Note.—The nozzle of each pipette should be unbroken.

Directions.—1. Carefully counterpoise a beaker, and run into it the water from a properly charged pipette. While the water is passing out, the nozzle should rest against the side of the beaker and remain there 15 sec. to drain. Find the weight and temperature of the water.

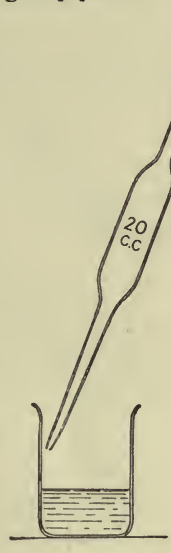

Fig. 6

To charge the Pipette.—Suck up the water above the mark and quickly cover the top with the finger tip. Remove the nozzle from the liquid, hold the pipette vertically, and let the excess drop out slowly till the bottom of the meniscus is level with the mark.

2. Repeat the operation three or four times, varying the number of seconds allowed for draining, and, if necessary, blowing out the residual water.

3. Make a note of the method yielding the best result for each instrument. This can be found from the data previously given. Thus, a 25-cu.-cm. pipette should deliver 24.95 grm. of water at 15°.

The following results were obtained by a student:—

Pipette, 25 cu. cm. Temperature of water, 14°.

After draining 15 sec.	24.959 grm.
Blowing out—giving no time to drain	24.957 ,,
Draining 15 sec. and blowing out ...	25.005 ,,

Evidently draining only was sufficient with this instrument.

Exercise 4.—Test the accuracy of your burette.

Directions.—1. Clamp the instrument vertically and fill it with cold distilled water. Use a funnel to avoid wetting the outside.

2. Squeeze the air out of the rubber tubing just above the pinchcock, and wash out the remainder by allowing the water to flow rapidly from the nozzle. This is important. The air in the nozzle is more easily displaced by inverting it, as shown in fig. 7. Fill up again and remove funnel.

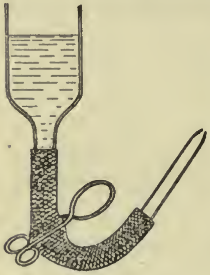

Fig. 7

3. Let the water drop out until the bottom of the meniscus falls to the first mark. The eye also must be exactly at the same level. (See notes at end of chapter.)

4. See that no leakage occurs at tap or pinchcock, and that no water is trickling down the outside of the burette.

5. Counterpoise, or weigh, a beaker, and deliver into it the first 10 cu. cm. from the burette, allowing a few seconds for the water to drain down before finally reading. Find the weight of the water. What should it be?

Note.—When a float is used it should be wetted with whatever liquid is being measured out, before dropping it into the burette. This will prevent air bubbles clinging to it, and consequent errors in reading.

6. Repeat 5, using the next 10 cu. cm. of water; and so on.

7. Measure carefully the lengths of those divisions tested, and compare them. Are they all equal?

A student got by the above method:—

0 cu. cm.	to	10 cu. cm.		...	9.990	grm.
10	,,	,, 20	,,	...	10.047	,,
20	,,	,, 30	,,	...	9.970	,,
30	,,	,, 40	,,	...	10.035	,,
40	,,	,, 50	,,	...	10.010	,,
				Total	50.052	,,

On filling up the burette again and running it out from 0.0 cu. cm. to 50 cu. cm., with only a slight wait for draining, the weight was found to be 49.96 grm. On repeating the test and allowing a much longer time for draining, the weight got was 50.07 grm. Evidently, with this instrument a *short* period of draining gives the best results.

Question 1.—Suppose you find the weight of water in each division of 10 cu. cm. approximately the same, whilst the divisions themselves are not equal, what conclusion would you draw? And what, supposing the divisions are found to be equal, whilst the successive weighings are found to increase or decrease?

Note.—As a rule the diameter of a glass tube decreases slightly in one direction.

Exercise 5.—Test the accuracy of the readings of graduated measuring cylinders.

Directions.—Since these are intended only for rough measurements, it will be sufficient to pour equal volumes of water successively into the cylinders, noting the reading after each addition. The volume of water chosen should bear a simple relationship to the measuring capacity of the vessel.

A student on adding four successive quantities of 25 cu. cm. from a pipette into a 100-cu.-cm. cylinder obtained the following readings: 25 cu. cm., 50 cu. cm., 75.3 cu. cm., 100 cu. cm. Thus, as is usually the case, the total volume shown was correct, whilst the intermediate readings were only approximately so.

NOTES ON READING THE HEIGHTS OF LIQUIDS

1. With a transparent liquid which wets the containing vessel, readings are usually made to the lowest part of the curved surface (meniscus). If the liquid is opaque, such as a solution of potassium permanganate, it is more convenient to read to the top edge.

2. In the case of a liquid like mercury, which does not wet or cling to the glass, it is usual to read to the highest part of the curved surface.

3. Whilst readings are being made, the vessel containing the liquid should be quite upright.

4. The eye must be on a level with the point being read, otherwise the reading may be inaccurate, as may be seen from the diagram (fig. 8).

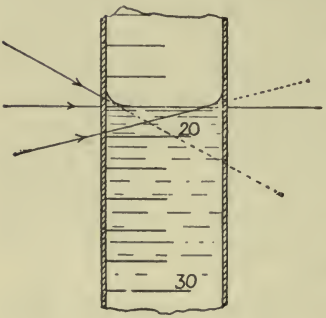

Fig. 8

CHAPTER III

Methods of ascertaining when Reactions are complete

When two solutions which react together have been mixed in such proportion that neither is in excess, the end-point of the reaction is reached. Practically this is assumed to be the case when only a trace of either remains unacted upon. It can be detected in various ways. There may occur a sudden *colour change* either in the reacting substances themselves, or in some other substance specially introduced, and called on this account an "indicator"; or, a *precipitate* may cease to form. Precipitation, however, seldom forms a good clue, since the approach of the end-point is apt to be obscured by turbidity, and sometimes the insoluble matter is not wholly thrown out of solution until much excess of the precipitant has been added, or until after some time has elapsed.

Of indicators, litmus is a good example; its change in colour is striking, and is brought about by mere traces of acid or alkali. Since it appears bright red in contact with acid and blue with alkali, a purple tint indicates the presence of neither; so that when this colour appears on adding alkali to a red acid solution, the end-point of the reaction between acid and alkali has been reached, and all further addition of alkali would be in excess. But whether an end-point is shown by colour change, or otherwise, practice in its detection is necessary to give that skill which exact work demands.

Cleansing Apparatus.—Before proceeding with our experiments it will be well to call attention to the necessity of using clean apparatus. All vessels should be cleansed, rinsed out with distilled water, and put away to drain dry immediately after use. Time spent in washing apparatus is thereby minimized, errors due to "dirty" apparatus are avoided, and corrosion and staining of the vessels are prevented.

DETECTION OF END-POINT

A. BY NOTING THE PROGRESS OF PRECIPITATION

Exercise 6.—Determine the end-point of the reaction between a definite quantity of sulphuric acid and barium chloride.

Directions.—1. Specially dilute a few cubic centimetres of the bench solutions of these reagents with four or five times as much distilled water.

2. Boil up 10 to 15 cu. cm. of the acid, and drop in the $BaCl_2$ cautiously as long as fresh precipitate appears to form.

3. Boil for a minute or more, then allow the liquid to clear.

4. Add further drops, one at a time, as long as each produces more cloudiness.

5. *Test your result.*—Decant some of the clear liquid (or filter if necessary) and divide into two parts: (*a*) and (*b*). Test (*a*) for free H_2SO_4 with litmus, also by noting whether milkiness appears on adding more $BaCl_2$. Test (*b*) for excess of $BaCl_2$ by noting whether it becomes milky on adding Na_2CO_3 or more H_2SO_4. What do you find?

Exercise 7.—Determine the end-point of the reaction between some ferric chloride and sodium hydroxide.

Directions.—1. Use very dilute solutions.

2. Boil up the $FeCl_3$ solution, and add to it the NaOH, proceeding generally as in Ex. 6. Make notes on the colour changes you observe, together with any peculiarity connected with the precipitation of the ferric hydroxide, $Fe(OH)_3$

3. *Test your result.*—Filter, and stand the beaker on a white surface. A coloured filtrate shows $FeCl_3$ to be still present. To a portion add either $K_4FeC_6N_6$ or NH_4NCS, and account for what you observe.

A colourless filtrate may contain excess of NaOH. For its detection use one drop of phenolphthalein. A pink colour shows the presence of alkali.

B. BY OBSERVING A COLOUR CHANGE IN ONE OF THE REAGENTS

Exercise 8.—Find the end-point of the reaction between a definite quantity of potassium permanganate and sulphuretted hydrogen.

Directions.—1. Use some fairly strong solution of $KMnO_4$, and dilute a fresh solution of H_2S to twice its bulk.

2. Test each solution with litmus paper and note what you observe. The highly-coloured $KMnO_4$ can be washed

off the paper. (If a burette is used for the $KMnO_4$, it should have a glass stopcock.)

3. *Test the result of your determination* by filtering off precipitate and noting whether the filtrate is (*a*) *colourless*, and therefore contains no excess of $KMnO_4$; (*b*) *odourless*, and consequently contains no free H_2S.

4. Let pieces of red and blue litmus paper lie in the filtrate for some time, and account for what you find. Compare with observation in 2.

5. Repeat the exercise after acidifying the $KMnO_4$ with about half its volume of dilute H_2SO_4. The filtrate may be tested for excess of H_2S with $AgNO_3$. Ag_2S is black; Ag_2SO_4 is white.

Question 2.—What difference does the addition of sulphuric acid make to the reaction? Write equations, expressing what has happened both with and without acid.

Exercise 9.—Try to find the end-point of the reaction between potassium dichromate and sulphur dioxide solutions (sulphurous acid).

Directions.—Test both with litmus paper, and state what you find.

Question 3.—Do you find it necessary to add sulphuric acid in order to keep the liquid clear?

Question 4.—Can you suggest a method of ensuring completion of the reaction in Ex. 9 without having any excess remaining of either original substance? State any change in colour noted, and write an equation expressing the reaction which has taken place.

C. BY OBSERVING THE COLOUR CHANGE OF AN INDICATOR

Exercise 10.—Find the end-point of the reaction between some common salt and silver nitrate.

Directions.—1. Use very dilute NaCl solution, to avoid waste of $AgNO_3$.

2. First, try to determine the end-point by noting when precipitation of AgCl ceases. The precipitate will clot on shaking well, especially after adding a little dilute HNO_3 or a few drops of CS_2.

3. *Test the result.*—Filter, and add each reagent to separate portions of filtrate. There should be no fresh precipitate in either case.

4. Find the effect of adding one drop of K_2CrO_4 solution to fresh portions of each reagent. *Note.*—Both should be quite neutral.

5. To that in which a red precipitate occurs, add NaCl, and shake up. If no permanent change is noted, add more chloride, and shake again.

6. From your observations, make use of K_2CrO_4 in order to make a more accurate determination of the end-point. Remember that AgCl is somewhat soluble in presence of NaCl.

Question 5.—What is the red precipitate in Ex. 10? Explain what happened on adding sodium chloride.

Question 6.—What may be observed when, to a mixed solution of sodium chloride and potassium dichromate, silver nitrate is added in excess? What conclusion do you draw from the permanence of the red precipitate?

CHAPTER IV

Common Indicators

A. INDICATORS FOR DETECTING ACIDS AND ALKALIS

To be a good indicator, a substance should become coloured when in the presence of traces of the substance to be detected. Its colour should be easily distinguished, and any change in colour should be sharp and capable of instant recognition. It is well to become acquainted with more than one indicator of a substance, since the colour of one may be affected by the presence of other substances, and the same colours cannot be distinguished equally well by different persons. Of the substances used to detect acids and alkalis the commonest are litmus, methyl orange, phenolphthalein, and turmeric. They are all organic compounds of complex structure.

Exercise 11.—Prepare a purple solution of litmus.

Directions.—1. Crush up 10 grm. of granular litmus, and stir it into 100 cu. cm. of hot water. Allow the undissolved particles to settle, and decant the extract.

2. Digest the residue with about the same quantity of hot water for an hour. After settling, add the two extracts and put by till next day.

3. Decant, or, if necessary, filter off the clear liquid, which will probably be blue. Add specially diluted HNO_3, a drop at a time, till a delicate purple tint is got.

4. Keep the prepared solution in an *open* bottle.

Fig. 9 shows a suitable arrangement. The cork forms a loose cap on the rim of the bottle, and is pierced by a simple pipette; i.e. a tube about six inches long nearly fused up at the lower end. Adjust it to withdraw a suitable volume of liquid.

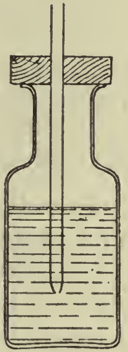

Fig. 9

Preservation of the solution.

(i) To prevent growth of mould, add a few crystals of phenol or a few drops of chloroform. Does phenol—or "carbolic acid" as it is commonly called—show an acid reaction with the litmus?

(ii) To restore the colour, should it fade, expose the liquid to the free air in an open dish.

Exercise 12.—Examine the behaviour of litmus with various substances.

Directions.—1. Besides ordinary acids and alkalis, test it with boric, phosphoric, and some organic acids. Also with solutions of such salts as borax, disodium phosphate, sodium carbonate, and sodium bicarbonate. Also with lime-water, sulphuretted hydrogen solution, distilled water that has been exposed in the laboratory, and some that has just been made, and solution of carbon dioxide.

Note.—In making a solution of carbon dioxide, see that no acid used to generate the gas is allowed to pass over with it. Bubble the gas slowly through water contained in a wash bottle, and make the solution with the washed gas.

2. Boil some solution of carbon dioxide, to which litmus has been added, as long as any change in colour occurs.

3. Make notes of your observations, and as far as possible account for what you have seen.

Exercise 13.—Prepare a solution of methyl orange, and examine its behaviour with acids, alkalis, &c.

Directions.—1. Dissolve 0.1 grm. in 100 cu. cm. of distilled water, and keep in a bottle fitted with a cork carrying a simple pipette. (See fig. 9.)

2. Find the effect of the solution on litmus paper.

3. Place *one drop* in each of two flasks containing about 50 cu. cm. of water and standing on a white surface. Make the water in one of the flasks slightly acid; afterwards make it alkaline. (This may be known by its effect on litmus paper.) Compare the colours obtained with that of the neutral liquid.

4. Try the effect on the indicator of such substances as those named in Ex. 12, especially some carefully-prepared solution of carbon dioxide.

Question 7.—How do the indications of litmus and methyl orange differ with respect to solution of carbon dioxide? (We may assume the presence of carbonic acid in this solution.)

Exercise 14.—Prepare a solution of phenolphthalein, and examine its behaviour with acids, alkalis, &c.

Directions.—1. Dissolve 0.5 grm. of the solid in 50 cu. cm. of alcohol and keep in a corked bottle. The cork may carry a simple pipette. (Fig. 9.)

2. Try the effect of one drop of the indicator on solutions of the following: Mineral and organic acids, alkalis, alkaline carbonates both normal and acid.

3. To a solution of acid sodium carbonate add one drop of phenolphthalein, and heat. Cool, and then pass carbon dioxide—washed free from acid—into the solution until a decided colour change occurs.

4. To a solution of ammonia add a drop of the indicator. Now dilute with water until the colour just disappears. Can you detect the presence of the gas by its odour? Add a few drops of purple or reddish litmus.

Question 8.—In what general way does phenolphthalein differ from the two indicators previously examined? How could you make use of your observations of its behaviour with acid sodium carbonate? Did you find the coloration due to caustic soda permanent?

Exercise 15.—Examine the behaviour of turmeric with alkalis and acids.

Directions.—1. Use turmeric paper; i.e. paper strips which have been soaked in an alcoholic extract of the colouring matter and dried. Dip some strips into very dilute alkali, and dry them, noting the colour changes.

2. Try the effect of ordinary acids and alkalis upon turmeric; also coloured liquids, such as vinegar, potassium manganate, and permanganate; also saliva.

Question 9.—Do turmeric and litmus give the same indications with saliva?

B. INDICATORS FOR DETECTING OTHER SUBSTANCES. EXTERNAL INDICATORS

Starch, especially when in solution, is an excellent indicator for free iodine.

Potassium dichromate ($K_2Cr_2O_7$) has already been used as an internal indicator in the reaction between a silver salt and a haloid. (Ex. 10.)

Where *coloured* liquids are concerned it is obviously impossible to use indicators in the way previously considered. For instance, the indications afforded by a solution of litmus when added to common vinegar can scarcely be relied upon to show when sufficient alkali has been added to neutralize the acid of the vinegar. A bit of litmus paper dropped into the vinegar will do so, but not sharply. A better way is to apply small drops of the acid liquid, withdrawn at short intervals, either to a piece of the purple paper laid on the bench, or to drops of purple litmus solution previously placed upon a white tile. By this means not only can neutralization be detected, but also its approach. Indicators when used in this way are distinguished as "external", or as "drop reagents". The end-points of many reactions can be detected by their means, but some practice is necessary to obtain results as accurate as with internal indicators. Two external indicators in very common use are iodized starch paper and potassium ferricyanide.

Exercise 16.—Prepare a "starch solution" and examine its behaviour with iodine.

Directions.—1. Mix 1 grm. of potato starch, or, better, "soluble" starch, with 10 cu. cm. of cold water, and pour into it about 200 cu. cm. of boiling water. Should a milky appearance persist, boil up for two minutes—not longer, or the starch will be converted to dextrose.

2. Filter off cloudy matter.

3. Add 1 cu. cm. of the clear solution to some water, and then one drop of solution of iodine. Boil some of the blue "iodide of starch" obtained, for a minute or two; allow to cool, and state what happens.

4. To some dilute iodine solution add sodium thiosulphate ($Na_2S_2O_3$) drop by drop, till the colour just disappears. Add 1 cu. cm. of starch solution. Was all the iodine used up?

5. Find the effect of $Na_2S_2O_3$ on some of the iodide of starch obtained in 3. (See note on Ex. 16, p. 151.)

Exercise 17. — Prepare some "iodized starch paper", and with it determine when sufficient chlorine water has been added to some sodium arsenite solution to oxidize it to arsenate.

Directions.—1. *To prepare the paper.*—Dissolve about 0.5 grm. of pure KI in 100 cu. cm. of the starch solution prepared in Ex. 16. Soak some clean white filter paper in it, dry, and cut into strips. Preserve it (from chlorine and other fumes) in a well-corked bottle.

2. *To examine the effect of each reagent on the indicator.*—(i) Moisten a strip with pure water; place a drop of each solution upon it at different places, and note. *N.B.*—Withdraw the solutions on separate, clean, thin glass rods. (ii) See whether very dilute chlorine water produces the same effect as a concentrated solution.

3. *To determine the end-point.*—Drop the chlorine water —preferably from a burette—into the arsenite solution until a drop of the liquid withdrawn on a rod, and applied to the starch paper, produces a faint blue colour. Shake up after each addition of chlorine water. Take care that *the successive drops touch different parts of the paper.*

4. Try the reverse process, viz. that of adding the arsenite to chlorine water till the end-point is reached. Which do you consider the better method? (See note on Ex. 17, p. 151.)

Exercise 18.—Oxidize some ferrous sulphate to the ferric state by means of potassium dichromate. Determine the end-point of the reaction with potassium ferricyanide.

Directions.—1. Try the effect of one of the substances upon each of the others.

(i) Add $K_2Cr_2O_7$ solution to $FeSO_4$ solution.

(ii) Repeat (i) after acidifying the iron solution with dilute H_2SO_4.

(iii) Add freshly-prepared solution of ferricyanide ($K_3FeC_6N_6$) to solutions of (*a*) $FeSO_4$; (*b*) $K_2Cr_2O_7$; (*c*) $FeCl_3$ or other ferric salt.

(iv) Add $K_2Cr_2O_7$ drop by drop to $FeSO_4$ solution previously acidified, and containing one or two drops of the indicator. Does the blue colour disappear when $K_2Cr_2O_7$ is added in excess?

2. *Determine the end-point.*

(i) Place about a dozen separate drops of indicator on a white tile or plate.

(ii) Acidify a fresh portion of $FeSO_4$, and drop into it $K_2Cr_2O_7$ until a bright-green solution is obtained. Shake the mixture. Withdraw a drop on the end of a thin glass rod, and mix it with one of the drops of $K_3FeC_6N_6$. A blue colour shows ferrous salt to be still present. Add more $K_2Cr_2O_7$ and test again, repeating until the blue colour fails to appear.

Question 10.—Could you detect the end-point—or completion of oxidation of the ferrous salt—without using the indicator? Give your reasons.

Question 11.—What is the blue precipitate obtained with the indicator?

Question 12. What inference would you make if the liquid produced in Ex. 18, 2, became *yellowish* green? And what indication is there in the successive trials that the end-point is being approached?

N.B.—Some notes on indicators will be found in Chapter XI.

CHAPTER V

Standard or Volumetric Solutions

A standard or volumetric solution is made with water and usually contains a known weight of some definite chemical substance in 1 cu. cm. This weight is termed the "strength of the solution". Sometimes the term refers to the weight of some other substance with which 1 cu. cm. of the solution reacts.

The strength of volumetric solutions is low: usually there is less than one molecular or formula weight in grammes per litre. When exactly this quantity is present, the solution is sometimes spoken of as a "molecular" or "molar" solution. Most volumetric solutions contain no more than one-tenth of this weight of solute to the litre; as, while yielding results as accurate as more concentrated solutions, they are found more convenient to work with.

The strength of a "molar" solution of caustic soda is given thus:—

$$1 \text{ cu. cm.} = 0.04001 \text{ grm. } NaOH,$$

because 1 cu. cm. contains one-thousandth part of 40.01 grm. of the alkali whose formula weight is 40.01. [$O = 16$, $H = 1.008$, $Na = 23$.]

It is, however, far more common to use solutions of what is called "normal" strength, or those which bear some simple ratio to this value, such as decinormal, twice normal, &c., and to express their strength by the abbreviations N., $\frac{N.}{10}$, 2 N., &c.

A *normal* solution contains per litre either (i) a gramme equivalent of its solute, or (ii) that weight of it which can furnish in some special reaction the gramme equivalent of one of its constituents. It may, or may not, be molar.

Since the acidity of acids is due to hydrogen, normal solutions of these compounds will contain 1.008 grm. of the acid-forming hydrogen to the litre. As a consequence, molar and normal solutions of monobasic acids are the same; but normal solutions of dibasic acids are semi-molar, and those of tribasic acids are one-third molar strength.

Of *hydrochloric acid* (HCl), a molar solution contains 36.468 grm. of hydrogen chloride per litre—36.468 being its molecular weight; and a normal solution contains the same weight because it includes the gramme equivalent (1.008) of acid-forming hydrogen per litre.

Of *sulphuric acid* (H_2SO_4), a molar solution contains 98.086 grm. of hydrogen sulphate per litre; but a normal solution contains only half this weight or 49.043 grm., since the former solution contains two gramme equivalents of acid-forming hydrogen.

With regard to *alkalis*, 1 l. of normal solution must contain that weight of alkali which can exactly neutralize 1 l. of normal acid; that is, it must contain the gramme equivalent both of the metal and of hydroxyl; for the metal replaces 1.008 grm. of hydrogen to form the salt, while the hydroxyl unites with this hydrogen to form water. This will be seen from the following equation:—

$$\underset{\underbrace{1.008 + 35.46}_{36.468}}{\mathrm{HCl}} + \underset{\underbrace{23 + 16 + 1.008}_{40.008}}{\mathrm{NaOH}} = \underset{\underbrace{23 + 35.46}_{58.46}}{\mathrm{NaCl}} + \underset{\underbrace{1.008 + 16 + 1.008}_{18.016}}{\mathrm{HOH}}$$

It follows that equal volumes of normal acid and alkali neutralize each other when mixed.

Normal *caustic soda* (NaOH) therefore must contain 40.008 grm. of sodium hydroxide, or 23 grm. of sodium to the litre, as these weights are necessary to displace the equivalent weight (1.008 grm.) of hydrogen from an acid. The equation shows that a molar solution is of the same strength.

Similarly, it will be found that normal and molar solutions of potassium hydroxide (KOH) and ammonia (NH_3) respectively are of the same strength.

It must be remembered that acids may contain hydrogen which is quite independent of that conferring acid properties. Only one-fourth of the hydrogen in acetic acid ($C_2H_4O_2$) is so concerned, and its formula is usually written $CH_3.COOH$ to express this fact. Only the hydrogen in the carboxyl group (COOH) is acid-forming. That of the methyl group (CH_3) is not so; for the acidity of acetic acid is not lessened when this hydrogen is wholly replaced by chlorine. N. acetic acid therefore contains a mol of the acid to the litre.

The following points should be well noted, as they may aid you considerably to shorten your work when using standard acids and alkalis:—

1. Normal acid solution exactly neutralizes an equal volume of normal alkali.

2. Normal solutions of acids are of equal "strength", for they can all neutralize an equal volume of any

normal alkali. [Equal volumes of N. acids contain the same weight of acid-forming hydrogen and equivalent weights of acid.]

3. Normal solutions of alkalis are also of equal strength, as they can all neutralize an equal volume of normal acid. [Equal volumes of N. alkalis contain the same weight of hydroxyl and equivalent weights of metals.]

4. The statements under 2 and 3 equally apply to decinormal and other solutions of corresponding strength.

5. The gramme equivalent of an acid contains 1.008 grm. of that hydrogen replaceable by a metal.

6. The gramme equivalent of a base is that weight which neutralizes a gramme equivalent of acid, and can provide 17.008 grm. of hydroxyl to unite with the displaced hydrogen.

Besides acids and alkalis, standard solutions of "*salts*" are used. A mixture of 1 l. of N. HCl and 1 l. of N. NaOH yields 2 l. of sodium chloride solution, containing only one gramme equivalent each of sodium and chlorine. This solution is therefore seminormal. In calcium chloride ($CaCl_2$) there are two equivalents of chlorine united with the calcium; and in its reaction with sulphuric acid two equivalents of hydrogen are displaced by the metal.

$$CaCl_2 + H_2SO_4 = CaSO_4 + 2\,HCl.$$

A solution containing the gramme formula weight of this salt to a litre is, therefore, of 2 N. strength.

Potassium Permanganate ($KMnO_4$).—It may appear to a beginner that a normal solution of this salt should contain the gramme formula weight of the compound to the litre, since this includes an equivalent weight of potassium. This reagent, however, is not used for the potassium it contains, but for the oxygen it can part with; and it is this consideration which must guide us in determining the weight necessary to prepare a solution of any required strength. A normal solution, then, should contain that weight per litre which will yield the gramme equivalent of oxygen (8 grm.). An incautious student might assume that a normal solution should contain one-eighth of the gramme formula weight to a litre, since this weight contains 64 grm. of oxygen. He would be wrong, because *all* the oxygen of the compound is not parted with in its reactions with other substances.

The formula of the salt used to be written $K_2Mn_2O_8$, and we may conceive it to be made up of two oxides, K_2O and Mn_2O_7, the former basic and the latter acidic. The heptoxide of manganese readily parts with a large proportion of its oxygen to reducing agents, and the products suggest that the salt breaks up thus:—

$$\underbrace{K_2O,\ Mn_2O_7}_{316.1} = K_2O + 2\,MnO + \underbrace{5\,O}_{80}$$

for 80 grm., or ten gramme equivalents of oxygen can be obtained from 316 grm. of the permanganate. If sulphuric acid is present, the precipitation of oxide of manganese is prevented by its conversion into sulphate. The break-up of the permanganate may then be represented—

$$\underbrace{2\,KMnO_4}_{316.1} + 3\,H_2SO_4 = K_2SO_4 + 2\,MnSO_4 + 3\,H_2O + \underbrace{5\,O.}_{80}$$

A litre of N. permanganate should contain only 31.61 grm. of the salt, because this weight can yield 8 grm.

of oxygen to a reducing agent. It is usual, however, to make permanganate solution of *decinormal* strength for reasons which will be given later.

$\frac{N.}{10}$ Potassium permanganate.

1 cu. cm. = 0.003161 grm. $KMnO_4$
1 cu. cm. = 0.0008 grm. oxygen.

Potassium dichromate ($K_2Cr_2O_7$) is also largely used for the same purpose as permanganate, as, like the latter, it easily parts with a portion of its oxygen to reducing agents. We may consider this compound also to be made up of basic and acidic oxides, K_2O with two of CrO_3. The latter readily give up a portion of their oxygen and pass into the chromous condition

$$\underbrace{K_2O,\ 2\,CrO_3}_{294.2} = K_2O + Cr_2O_3 + \underbrace{3\,O}_{48}.$$

This agrees with the fact that 48 grm. of oxygen are obtainable from 294.2 grm. of the salt. Evidently, therefore, a normal solution should contain one-sixth of this weight of the salt to the litre, viz. 49.03 grm., as this will yield the necessary 8 grm. (the gramme equivalent) of oxygen. Acid is used with this reagent for the same purpose as with permanganate.

$$\begin{aligned}&K_2O,\ 2\,CrO_3 + 8\,HCl\\&\quad = 2\,KCl + 2\,CrCl_2 + 4\,H_2O + 3\,O.\end{aligned}$$

The above examples will serve to illustrate the principles by which we must be guided in making our standard solutions.

Preparation of Standard Solutions.—The solvent is usually water, and the process is generally simple when we are sure of the composition of the substance to be dissolved; for, since the strength of a solution depends upon the weight of solute taken and the volume of solution made, reasonable accuracy in weighing and measuring is all that is required. When the purity of the substance is doubtful, it is usual to take such an excess as shall make a solution above the strength required; ascertain its exact value by titration against some other solution already standardized, then dilute it with sufficient water to give it the required value. For example, decinormal caustic soda should contain 4.001 grm. of NaOH to the litre. But ordinary caustic soda does not consist wholly of NaOH; there is usually present more or less water, and possibly silica, alumina, &c., besides. Should it be labelled "90% NaOH", at least $\left(4.001 \times \frac{100}{90}\right)$ grm. must be taken to make a litre of approximately decinormal strength. But as an over-strong solution is easily reduced by suitable dilution with water, we take more than this, say 4.5 to 5 grm., which should provide a solution something above decinormal. Its exact strength can be determined with standard acid, and sufficient water can then be added to make it exactly decinormal. Suppose the strength is found to be 1 cu. cm. = 0.0042 grm. NaOH; then a small quantity of $\frac{N.}{10}$ solution can be made by diluting 40 cu. cm. (or, more exactly, 40.01 cu. cm.) to 42 cu. cm; for—

1 cu. cm. original solution = 0.0042 grm. NaOH,
1 cu. cm. $\frac{N.}{10}$,, = 0.004001 grm. NaOH

$\therefore \frac{40}{42}$ cu. cm. original solution will contain as much NaOH as 1 cu. cm. $\frac{N.}{10}$ solution. So $\frac{40}{42}$ cu. cm.

should be diluted to 1 cu. cm.; or, to put it practically, 40 cu. cm. to 42 cu. cm., and other volumes in the same proportion. Suppose it is required to make half a litre of $\frac{N.}{10}$ solution; what volume of the original solution should be measured out for dilution? Evidently that which contains (0.004001 × 500) grm. (2.0005 grm.). This weight is contained in $\frac{2.0005}{0.0042}$ cu. cm. (476.3 cu. cm.) of the original solution. To make the half-litre of the solution required, this volume should be carefully measured out into a half-litre flask and diluted with distilled water up to the mark. Thorough mixing should take place before the reading is finally made. With $\frac{N.}{10}$ and similar dilute solutions, however, no practical error arises if 23.7 cu. cm. of water are directly added to the 476.3 cu. cm. of solution measured out; although it should be remembered that when strong solutions are used the volume obtained after dilution is not necessarily equal to the sum of the original volumes. Should a solution be made too dilute for our purpose, time will usually be saved by making a fresh one altogether; for the operations involved in strengthening a weak solution, such as evaporating down, cooling, &c., are lengthy.

Most volumetric solutions are made of decinormal strength, as they are sufficiently strong for the usual estimations. Old solutions should have their strength redetermined before use, since many are apt to suffer decomposition either from the effects of light, oxidation by air, or by reaction with laboratory fumes or with some ingredient of the containing vessel.

If we know the relative proportion by weight in which two substances react, and the strength of a solution of one of them, all that is necessary to determine the strength of a solution of the other is to ascertain accurately the volumes which must be mixed together to arrive at the end-point of the reaction. The process is referred to as "titration". If we also know the weight of substance dissolved in the solution titrated, the ratio of that found to that dissolved should express the degree of purity of the substance.

Suppose we require to know the strength of a solution of caustic soda, made as above, approximately of $\frac{\text{N.}}{10}$ strength, and are provided with $\frac{\text{N.}}{10}$ HCl, 20 cu. cm. of which neutralize 25 cu. cm. of the alkali solution.

The equation—

$$\underbrace{\text{HCl}}_{36.5} + \underbrace{\text{NaOH}}_{40.01} = \text{NaCl} + \text{H}_2\text{O}$$

shows that 36.5 parts by weight of HCl = 40.01 parts of NaOH. Now—

1 cu. cm. of the acid = 0.00365 grm. HCl,
20 cu. cm ,, = 0.073 ,,
Therefore 0.073 grm. HCl requires for its neutralization (or =)

$$0.073 \times \frac{40.01}{36.5} \text{ grm. NaOH,}$$

and experiment has shown that this weight is contained in 25 cu. cm. Therefore 1 cu. cm. of the caustic soda $= \left(0.073 \times \frac{40.01}{36.5} \times \frac{1}{25}\right)$ grm. or 0.0032 grm. NaOH. The solution being $\frac{0.0032}{0.0040}$ of decinormal strength it may be described as 1 cu. cm. $= \frac{4}{5} \times \frac{\text{N.}}{10}$ NaOH; and it will be evident that in neutralizing power 5 cu. cm. will have the same effect as 4 cu. cm. of $\frac{N.}{10}$ solution.

Question 13.—What is a standard solution?

Question 14.—What do you understand by "strength of a solution"?

Question 15.—Give the gramme equivalent of hydrochloric and sulphuric acids, caustic potash, and calcium hydroxide.

Question 16.—A "normal" solution is said to be a special standard solution. Why?

Question 17.—What weight of hydrogen nitrate is equivalent to a gramme formula weight of (*a*) hydrogen chloride, (*b*) oxalic acid [$(COOH)_2$], (*c*) barium hydroxide, (*d*) ammonia?

Question 18.—Which indicator would you prefer in determining when acetic acid is neutralized?

Question 19.—Which indicator should be avoided in finding the strength of an ammonia solution by means of standard acid?

Question 20.—In standardizing an acid with $\frac{N.}{10}$ Na_2CO_3, which indicator would you select? and why?

Question 21.—Calculate the weight of substance dissolved in each of the following:—

(*a*) 35.5 cu. cm. $\frac{N.}{10}$ HCl.

(*b*) 14.2 cu. cm. N. H_2SO_4.

(*c*) 25.0 cu. cm. $\frac{N.}{10}$ NH_3.

(*d*) 50.0 cu. cm. $\frac{N.}{25}$ $Ca(OH)_2$.

(*e*) 18.4 cu. cm. $\frac{N.}{2}$ Na_2CO_3.

Question 22.—90 cu. cm. of N. H_2SO_4 were required to neutralize 100 cu. cm. of ammonia solution. Find the weight and volume at S.T.P. of the gas dissolved in 1 l.

CALIFORNIA COLL
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CHAPTER VI

Acidimetry and Alkalimetry

All volumetric determinations of the weight of acid present in a solution are included under "acidimetry". "Alkalimetry" includes all similar determinations of alkalis. The indicators commonly used in these processes have already been referred to. They are litmus, methyl orange, and phenolphthalein.

Before carrying out an estimation, note the following points carefully:—

1. In titrating mineral acid against alkali either litmus, phenolphthalein, or methyl orange may be used.

2. *Litmus* is generally useful in titrating ordinary inorganic acids and bases against each other; also with ammonia and oxalic and benzoic acids. Its indications are unreliable with phosphoric and sulphurous acids, and if carbonates are present all liberated carbon dioxide must be expelled before determining the end-point.

3. *Methyl orange* is most suitable when hydrochloric, sulphuric, or other "strong" acid (excepting hot nitric acid) is being titrated against a "weak" base, and is especially useful in estimations where carbon dioxide is set free, as its indications are not affected by the presence of this compound. Neither is it affected by boric acid; hence it can be used in

estimating borax by mineral acid. On the other hand. its sensitiveness is lessened by the presence of certain salts, and nitrous acid decomposes it.

4. *Phenolphthalein* should be chosen when a "strong" base is to be titrated against a "weak", acid, especially organic acids. With ammonia its indications are unreliable.

5. *In very dilute solutions* the compounds formed by indicators suffer more or less hydrolysis, and the sharpness of the colour change consequently suffers.

6. In making estimations, *strictly comparable results* can be obtained only when the titrations are carried out in the same order: the acid should always be run into the alkali, or the alkali always into the acid.

DIRECT METHOD

Exercise 19. — Find the number of cubic centimetres of bench hydrochloric acid (dilute) necessary to neutralize 25 cu. cm. of bench caustic soda.

Directions. — 1. Before titrating, dilute both solutions equally by making up 50 cu. cm. of each to 250 cu. cm. with distilled water, and shake up well.

2. Set up a burette. (See directions in Ex. 4, also "Burettes", Chapter II.)

3. Put the diluted HCl in burette. If wet inside, first wash out the instrument with some of the acid, and let it run away.

4. With pipette, measure out 25 cu. cm. of diluted NaOH into a suitable beaker or flask of about 200 cu. cm. capacity. If the pipette is wet inside it must be washed out with some of the NaOH to be titrated.

5. Stand the beaker on a white tile (or paper), and add litmus solution drop by drop till it makes the NaOH distinctly blue; but do not use more than is necessary.

6. *The Titration.*—First make a preliminary or rough

trial. Read and record the height of the acid in the burette, or of the mark on the float if one is used. Set the nozzle about level with the top of the beaker, and run in the acid a cubic centimetre or so at a time, stirring or shaking after each addition until excess is shown. Again read the height of acid and record.

Next, repeat the titration with a fresh quantity of alkali, running the acid straight into the alkali to within a cubic centimetre of the previous volume used. From this point proceed cautiously, adding one drop only after each stirring, until the litmus just turns red. Make all readings carefully to 0.1 cu. cm.; record them and the volume of acid used. Do two or three more titrations, carefully recording as before. Find the *average* volume of acid used for a titration, not including that of the rough trial, or any one which differs widely from the rest.

It is well to note the reading carefully *just before* the end-point is reached, in case the next addition of acid should furnish too great excess.

7. *The Record.*—It is a good plan to state the exercise clearly at the top of the right-hand page of your notebook. Underneath, state the method you adopt, giving the essentials in proper order, and also any observations you may make as you proceed. Necessary equations and the method of deducing your result may also be placed here. Let the opposite page be reserved for such records as weighings, readings of burette, working out calculations, &c.—all neatly set out. An example is given in full in Ex. 23.

Question 23.—How many cubic centimetres of the acid solution should have been used if it is equal in strength to the alkali?

Question 24.—If 26.4 cu. cm. of acid were used to neutralize 25 cu. cm. of alkali, which is the "stronger" solution? Give their relative strengths.

Question 25.—A and B respectively found 15 cu. cm. and 17.5 cu. cm. of the nitric acid supplied to them necessary to neutralize the same quantity of caustic potash. Compare the strengths of the acid solutions supplied.

Exercise 20.—Find the number of cubic centimetres of dilute sulphuric acid necessary to neutralize 25 cu. cm. of dilute caustic soda.

Directions.—See Ex. 19.

Question 26.—Compare the neutralizing powers of the sulphuric acid and hydrochloric acid.

Exercise 21.—Prepare about 6 grm. of pure dry sodium carbonate (normal) from the bicarbonate.

Directions.—1. Calculate the approximate weight of bicarbonate which should be taken according to the equation—

$$2\,NaHCO_3 = Na_2CO_3 + CO_2 + H_2O.$$

(See note on p. 151.)

2. Heat the $NaHCO_3$ for half an hour in an air oven at 280°; or, if this is not available, heat it to dull redness for 20 min., occasionally stirring. Cool in exsiccator and weigh. Heat again for 5 min.; cool and weigh again. Repeat, if necessary, till two consecutive weighings agree. A porcelain dish may be used. Record all weighings.

3. Keep the Na_2CO_3 in exsiccator till used for next exercise.

Exercise 22.—Make 100 cu. cm. of normal sodium carbonate, and keep for future use.

Directions.—1. A litre of N. Na_2CO_3 should contain the gramme equivalent of the metal.

2. Weigh out the quantity necessary to make 100 cu. cm. on a watch-glass, and transfer it to a 100-cu.-cm. graduated flask. Loss in transference may be prevented by using a *dry* funnel with fairly wide stem. If wet, the water will unite with the Na_2CO_3 to form the hydrated salt and block up the stem. Wash down the last particles with a jet of water.

3. Completely dissolve the carbonate, and take care that the solution is quite cold before adding water up to the mark.

4. Keep the solution in a corked bottle labelled "N. Na_2CO_3", or "1 cu. cm. = 0.053 grm. Na_2CO_3". (See note on p. 151.)

Exercise 23.—Make 250 cu. cm. of $\frac{N.}{10}$ Na_2CO_3 by diluting some of the normal solution, and with it determine the weight of hydrogen chloride in 1 l. of ordinary dilute acid.

Directions.—1. Accurately measure out from a burette or pipette 25 cu. cm. of N. Na_2CO_3 into a 250-cu.-cm. graduated flask. Add distilled water to the mark and mix thoroughly. Label the solution "1 cu. cm. = 0.0053 grm. Na_2CO_3", or "$\frac{N.}{10}$ Na_2CO_3".

2. Since volumetric work is apt to be more accurate when the solutions are approximately of equal strength, the acid should be further diluted to somewhere near $\frac{N.}{10}$.

To make a rough determination of the amount of dilution necessary, put, say, 2 cu. cm. of the acid with a drop of methyl orange (why not litmus?) into a graduated measuring-cylinder (100 cu. cm.), and pour into it $\frac{N.}{10}$ Na_2CO_3, a little at a time, with constant shaking until the yellow colour appears. Should the total volume now measure anywhere near 50 cu. cm., evidently the acid is about twenty-five times too strong; and 10 cu. cm. diluted to 250 cu. cm., and well mixed, will give a suitable solution to work with the $\frac{N.}{10}$ Na_2CO_3.

3. Using methyl orange as indicator, make four accurate titrations after a rough preliminary test, and find the average quantity used.

4. *Tabulate your results* on the left-hand page somewhat as shown below:—

		TITRATIONS.			
(A)	(rough) cu. cm.	(*a*) cu. cm.	(*b*) cu. cm.	(*c*) cu. cm.	(*d*) cu. cm.
Burette readings: (1)	1.4	0.3	0.5	0.8	0.0
Burette readings: (2)	28.5	26.75	27.0	27.35	26.5
Acid used	27.1	26.45	26.5	26.55	26.5

Average of four titrations, 26.5 cu. cm.

	Burette Readings. cu. cm.		Volume of Acid used. cu. cm.
or (B) TITRATIONS (rough)	1.4	28·5	27.1
1st	0.3	26.75	26.45
2nd	0.5	27.0	26.5
3rd	0.8	27.35	26.55
4th	0.0	26.5	26.5
			4) 106.00
Average volume of acid used			26.5

5. *Enter your results* on right-hand page somewhat as follows:—

Volume of $\frac{N.}{10}$ Na_2CO_3 used per titration ... 25.0 cu. cm.

Average volume of specially diluted HCl used 26.5 ,,

Weight of Na_2CO_3 used ... ... 0.0053 × 25 grm.

$$\text{Equation: } \underbrace{Na_2CO_3}_{106} + \underbrace{2\,HCl}_{2 \times 36.47} = 2\,NaCl + CO_2 + H_2O,$$

shows 106 grm. Na_2CO_3 = 72.94 grm. HCl.

$$\therefore (0.0053 \times 25)\text{ grm. } Na_2CO_3 = \begin{cases} \frac{72.94}{106} \times 0.0053 \times 25 \text{ grm.} \\ \text{HCl contained in 26.5} \\ \text{cu. cm. of the specially} \\ \text{diluted acid.} \end{cases}$$

∴ 1 cu. cm. of specially diluted acid

$$= \frac{72.94}{106} \times 0.0053 \times 25 \times \frac{1}{26.5} \text{ grm. HCl,}$$

and 1 cu. cm. of ordinary bench acid (dilute)

$$= \frac{72.94}{106} \times 0.0053 \times 25 \times \frac{1}{26.5} \times 25 \text{ grm. HCl.}$$

∴ 1 l. of this acid will contain

$$\frac{72.94}{106} \times \frac{0.0053 \times 25}{26.5} \times \frac{25 \times 1000}{1} \text{ grm. HCl,}$$

or 86.0 grm. HCl.

Question 27.—What volume of this dilute acid will be necessary to prepare half a litre of N. HCl?

Exercise 24.—Prepare 250 cu. cm. of N. hydrochloric acid from that whose strength you have just determined.

Directions.—1. Calculate the volume of acid necessary (to $\frac{1}{20}$ cu. cm.), and run this quantity from a burette (previously washed out with the acid) into a quarter-litre measuring-flask.

2. Add water to the mark, and mix well.

3. Keep in a bottle labelled either "N., HCl", or "1 cu. cm. = 0.03647 grm. HCl".

Calculation of Volume.—250 cu. cm. N. HCl must contain 0.03647 × 250 grm. HCl. If, as in previous example, 1 cu. cm. of the bench acid has been found to contain 0.086 grm. HCl, the number of cubic centimetres required will be—

$$\frac{0.03647 \times 250}{0.086} = 106.0 \text{ cu. cm.}$$

Exercise 25.—Prepare 250 cu. cm. of solution of HCl of approximately $\frac{N.}{10}$ strength by Dr. G. T. Moody's method.

Directions.—1. Place 50 to 100 cu. cm. of distilled water in the graduated flask, and fit it with a two-holed cork carrying an inlet tube, which must not quite reach the surface of the water, and an exit tube. Weigh flask with water, &c., carefully. (Fig. 10.)

2. Generate a steady stream of HCl by dropping concentrated H_2SO_4 upon NaCl, and pass the gas over into the graduated flask until about the necessary weight has been absorbed by the water. What should this weight be? The gas may pass some four or five minutes before the first weighing is made. (See note on p. 151.)

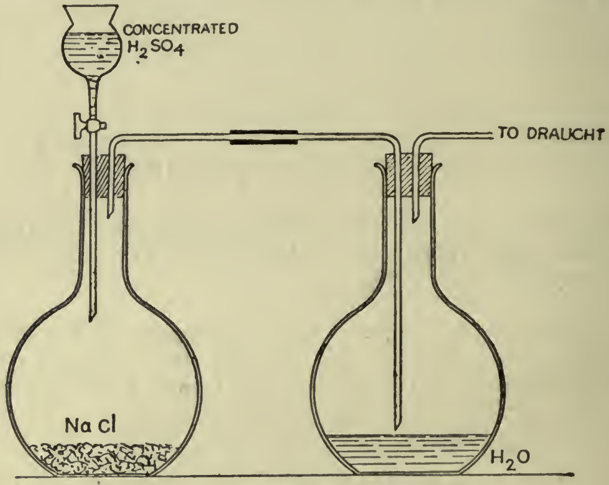

Fig. 10

3. Cool the solution before making the final weighing.

4. Add water to the mark, and mix well.

5. Calculate the strength of the solution, and make a note of it for comparison with what you find in the next exercise.

Note.—A solution somewhere near $\frac{N.}{10}$ strength may be made by filling a dry litre flask with HCl gas, and adding about 400 cu. cm. of water and shaking up.

Exercise 26.—Find the exact strength of the solution of hydrochloric acid made in Ex. 25 by titration against $\frac{N.}{10}$ Na_2CO_3. If it is found to be above $\frac{N.}{10}$, reduce it to this value by the addition of water. If below $\frac{N.}{10}$, express its relationship to $\frac{N.}{10}$ strength by means of a factor.

Directions.—1. The acid will be sufficiently near $\frac{N.}{10}$ strength for direct titration with $\frac{N.}{10}$ Na_2CO_3. Follow generally the directions for Ex. 23 to find its exact strength.

2. *To find the amount of dilution* necessary if the acid is above $\frac{N.}{10}$, see Ex. 24.

Note the following:—

(*a*) If 25 cu. cm. of $\frac{N.}{10}$ Na_2CO_3 require only 24.6 cu. cm. of the acid, it is evident that 24.6 cu. cm. contain as much HCl as 25 cu. cm. of $\frac{N.}{10}$ acid. Therefore to prepare $\frac{N.}{10}$ HCl, 24.6 cu. cm. should be diluted to 25 cu. cm., 98.4 cu. cm. to 100 cu. cm., and so on.

(*b*) If the strength of the acid is found to be 1 cu. cm. = 0.0038 grm. HCl, since 250 cu. cm. of $\frac{N.}{10}$ HCl must contain 0.003647 × 250 grm. HCl, the number of cubic centimetres of the overstrong acid necessary to provide 250 cu. cm. of $\frac{N.}{10}$ HCl will be—

$$\frac{0.003647 \times 250}{0.0038} = 239.9 \text{ cu. cm.}$$

(*c*) Where such dilute solutions as the above are used, and where only a few cubic centimetres of water are to be added, accuracy will not be impaired, and time will be saved, by running the requisite quantity of water into the dry graduated flask and filling up to the mark with acid.

3. *To find the factor.*

(*a*) Suppose 25.6 cu. cm. of the acid are necessary to neutralize 25 cu. cm. of $\frac{N.}{10}$ Na_2CO_3, the acid will be $\frac{25}{25.6}$ of $\frac{N.}{10}$ strength; i.e. $\frac{N.}{10} \times 0.976$.

(*b*) Suppose the strength of acid is 1 cu. cm. = 0.0034 grm. HCl. It may be represented as $\frac{0.0034}{0.003647} \times \frac{N.}{10}$, or $\frac{N.}{10} \times 0.932$, as $\frac{N.}{10}$ HCl contains 0.003647 grm. HCl in 1 cu. cm.

Question 28.—Two students preparing decinormal hydrochloric acid found, on titrating with $\frac{N.}{10}$ Na_2CO_3, that 21 cu. cm. of one solution (A) and 31.5 cu. cm. of the other (B) were required respectively to neutralize 25 cu. cm. of the alkali. Find the proportion in which the acids should be mixed in order to produce exactly $\frac{N.}{10}$ HCl.

To 21 cu. cm. of (A) 4 cu. cm. of water must be added to make $\frac{N.}{10}$ HCl, whilst 31.5 cu. cm. of (B) can supply 6.5 cu. cm. of water and remain of decinormal strength.

∴ 4 cu. cm. of water can be supplied by $\left(31.5 \times \frac{4}{6.5}\right)$ cu. cm., or 19.375 cu. cm., of (B), and remain $\frac{N.}{10}$. Consequently (A) and (B) should be mixed in the proportion 21 cu. cm. : 19.375 cu. cm.; or, more practically, 84 cu. cm. : 77.5 cu. cm.

Question 29.—Calculate the exact concentration (*a*) of hydrogen chloride in a solution marked N. × 1.045; (*b*) of sodium in a solution marked 1 cu. cm. = 0.06 grm. Na_2CO_3; (*c*) of sodium carbonate in a solution marked N. × 0.984.

Question 30.—How many cubic centimetres of a solution marked $\frac{N.}{10} \times 0{\cdot}975$ NaOH must be taken to neutralize 25 cu. cm. of $\frac{N.}{10}$ H_2SO_4?

Exercise 27.—Prepare 250 cu. cm. of approximately N. sulphuric acid from pure concentrated acid of specific gravity about 1·84.

Directions.—1. Make accurate weighings to enable you to do the next exercise.

2. Weigh a stoppered flask graduated for 250 cu. cm., and containing a little water. Note that the outside of flask is quite dry.

3. Drop 8 to 8.5 cu. cm. of concentrated H_2SO_4 into the flask without wetting the top part of the neck.

4. Cool under tap, dry thoroughly, then weigh again with stopper inserted, and find exact weight of acid used.

5. Add plenty of water; cool again, if necessary (to 15° C.), then finally fill to the mark, and mix well.

Exercise 28.—Ascertain the approximate concentration of hydrogen sulphate in the acid just prepared by finding its specific gravity and consulting tables.

Directions.—Find the specific gravity either (*a*) with a hydrometer, or (*b*) by ascertaining the exact weight (i) of a convenient quantity of the acid—say 25 cu. cm., and (ii) of the same volume of cold distilled water, and divide the former weight by the latter. Weighings to be made in a stoppered flask or specific-gravity bottle.

AQUEOUS SOLUTION OF H_2SO_4. (Lunge)

Specific Gravity.					Percentage of H_2SO_4 Present.
1.025	...	...	...	...	3.76
1.030	...	...	...	...	4.49
1.035	...	...	...	...	5.23
1.040	...	...	...	...	5.96
1.045	...	...	...	...	6.67

Exercise 29.—Find the exact strength of the sulphuric acid prepared in Ex. 27 by the following methods:—

Method A.—By titration against $\frac{N.}{10}$ Na_2CO_3.

Directions.—Follow generally those given for Ex. 23. It will be necessary to dilute the acid to about $\frac{1}{10}$th its present strength, so as to work well with $\frac{N.}{10}$ alkali.

Method B.—By neutralizing a known volume of the acid with ammonia, and finding the weight of ammonium sulphate produced. (M. Wenig.)

Directions.—1. Place 20 cu. cm. of the acid in a porcelain dish, add excess of AmOH, and evaporate to dryness on a water bath.

2. Heat to 120° in air oven till weight is constant.

3. Equation $2\,NH_3 + \underbrace{H_2SO_4}_{98.1} = \underbrace{(NH_4)_2SO_4}_{132.2}$ shows that the weight of H_2SO_4 in the acid taken is $\frac{98.1}{132.2}$ of weight of residue. How do your results agree?

Question 31.—Do you find the solution of acid above or below normal? How many cubic centimetres of water must be added to or withdrawn from 200 cu. cm. of the acid to make an exactly normal solution?

Question 32.—(*a*) Assuming the concentrated acid contained nothing but hydrogen sulphate and water, calculate the percentage of water present in it.

(*b*) How many molecules of water do there appear to be present for each molecule of H_2SO_4?

Exercise 30. — From the sulphuric acid whose strength has been determined make some exactly normal, and keep in a stoppered bottle properly labelled.

Exercise 31.—Prepare 250 cu. cm. of $\frac{N.}{10}$ sulphuric

acid, and with it determine the concentration of NaOH (or KOH) in your bench solution.

Directions.—1. Acid in burette.

2. Since the best results are obtained when the reacting solutions are approximately of equivalent strength, that of the NaOH should first be roughly determined, and then suitably reduced by the addition of water.

Pour 25 cu. cm. of the $\frac{N.}{10}$ acid into 100-cu.-cm. measuring-cylinder with a few drops of litmus, and add the alkali, a few drops at a time, with constant shaking till neutralization occurs. Suppose about 2 cu. cm. only of the alkali are necessary, it will be evident that if 2 cu. cm. are diluted to 25 cu. cm. or 20 cu. cm. to 250 cu. cm., the solution made will be somewhere near $\frac{N.}{10}$, as required.

Question 33.—A solution of caustic potash was found to contain 140.27 grm. of KOH to the litre.

(*a*) Express its relationship to N. by a factor.

(*b*) Some of the solution was diluted to $\frac{1}{10}$th its original strength, and 10 cu. cm. were then found sufficient to neutralize 30 cu. cm. of dilute nitric acid. Find the concentration of HNO_3.

(*c*) What dilution does the original alkali require to make it semi-normal?

Question 34.—30.3 cu. cm. of a solution of caustic soda were found necessary to neutralize 25 cu. cm. of N. H_2SO_4. How many cubic centimetres of water must be withdrawn from 100 cu. cm. of the alkali to make it normal?

Evidently the caustic soda is $\frac{25}{30.3}$ of normal strength; 30.3 cu. cm. contain only as much NaOH as 25 cu. cm. N. NaOH should contain, and so 5.3 cu. cm. of water must be withdrawn from 30.3 cu. cm. of alkali, and $\frac{5.3}{30.3} \times 100$ cu. cm., or 17.5 cu. cm. from 100 cu. cm.

Question 35.—How is water "withdrawn" from too weak a solution? What therefore do you consider to be the quickest way of making the N. solution?

Question 36.—Vessels containing standard caustic soda or other alkali are usually fitted with "calcium chloride" tubes. What is their use?

Why is it not usual to fit bottles containing alkali with glass taps or stoppers?

Exercise 32.—By means of a solution of ammonia of unknown strength, find the amount of dilution which concentrated hydrochloric acid has undergone to make ordinary dilute acid.

Directions.—Bench reagents are too strong for volumetric work, and both the ammonia solution and strong hydrochloric acid would lose perceptible quantities of their dissolved gases during titration.

1. Dilute 10 cu. cm. of bench NH_4OH to 200 cu. cm., and mix well.

2. Run 10 cu. cm. of the strong HCl from a burette into a 250-cu.-cm. graduated flask; add water, cool well, then fill to the mark. Label it $\frac{\text{"Strong HCl"}}{25}$.

3. Further dilute the dilute HCl of bench; 50 cu. cm. to 250 cu. cm. will do very well. Label it $\frac{\text{"Dilute HCl"}}{5}$.

4. Find the volume of each necessary to neutralize a definite volume of the diluted NH_4OH.

5. Indicator: litmus. Which indicator should *not* be used?

6. If the volumes of the first and second specially diluted acid are respectively x cu. cm. and y cu. cm., evidently $\frac{x}{5}$ cu. cm. of strong acid contain as much HCl as y cu. cm. of the dilute bench acid, and the relative strengths will be $y : \frac{x}{5}$.

Question 37.—If 24 cu. cm. N. H_2SO_4 are necessary to neutralize 20 cu. cm. of solution of ammonia, what volume of gaseous NH_3, measured at S.T.P., is dissolved in 1 l. of the solution?

$$\text{Solution of } NH_3 \text{ is } \frac{24}{20} \text{ N. strength.}$$

∴ 1 l. of solution will contain

$$17.034 \times \frac{24}{20}, \text{ or } 20.4408 \text{ grm.}$$

At S.T.P. the mol of a gas occupies 22.25 l. Since the mol of NH_3 is 17.034 grm, 20.4408 grm. will occupy—

$$\frac{204408}{170340} \times 22.25 \text{ l.}$$

Exercise 33.—The concentration of ammonia in the solution ordinarily used in the laboratory is one-fifth that of the original solution. Using $\frac{N.}{10}$ H_2SO_4 find (*a*) the weight of NH_3 contained in 1 l. of the original ammonia solution; (*b*) the volume this ammonia would occupy in the gaseous state at S.T.P.

Directions.—1. Dilute the ordinary bench solution of NH_3 still further, so as to work well with $\frac{N.}{10}$ H_2SO_4. The amount of dilution can be ascertained by a preliminary rough measurement as given in Ex. 31.

2. Acid in burette. Which indicator?

Question 38.—Why are standard solutions of ammonia less commonly kept in laboratories than those of caustic soda or potash?

Exercise 34.—Find the solubility of calcium hydroxide in water at the temperature of the laboratory by a volumetric method. Give your answer as the weight of $Ca(OH)_2$ contained in 100 cu. cm. of solution.

Directions. — 1. *Preparation of solution.* — Place some powdered slaked lime in 100 to 200 cu. cm. of water contained in a flask. Cork, and allow to stand half an hour or more with occasional shaking. Filter, and protect the lime-water formed from contact with air as far as possible. Why?

2. *Titration.*—Use $\frac{N.}{10}$ acid. Even H_2SO_4 may be used, as the sulphate formed is not precipitated, since it is rather more soluble than the hydroxide.

Question 39.—Find the strength of the solution of $Ca(OH)_2$. What relationship to N. does it bear?

LITMUS USED WITH A CARBONATE

Exercise 35.—Find the percentage of Na_2O in some soda carbonate crystals using $\frac{N.}{10}$ acid, and litmus as indicator.

Directions.—1. *To make a solution of suitable strength.*—Assume the crystals to agree approximately with the formula $Na_2CO_3, 10\,H_2O$. Since 1 l. of N. solution should contain 143 grm. of the pure substance (as this weight will contain the gramme equivalent of sodium), $3\frac{1}{2}$ grm. will be sufficient to make 250 cu. cm. of solution near $\frac{N.}{10}$ strength.

2. *Use of weighing-bottle.*—Place some roughly powdered crystals in a clean weighing-bottle (or test-tube), and find the exact weight of the whole. Tap out a little of the powder into the flask, avoiding any loss, until about the necessary weight has been transferred (this may be ascertained by roughly weighing at intervals); then find the exact final weight. The difference between this and the first weight gives the quantity taken.

3. Acid in burette.

4. Equation $\underbrace{Na_2O}_{62}.CO_2, + 2\,HCl = 2\,NaCl + CO_2 + H_2O$

furnishes the key necessary to determine the weight of Na_2O in the carbonate.

$$\frac{\text{Total weight of } Na_2O}{\text{Weight of crystals taken}} \times 100 \text{ gives the required answer.}$$

5. *Use of litmus when carbon dioxide is liberated.* (See Ex. 12.)—Dissolved CO_2 gives an acid reaction with litmus, and as this gas is liberated during the titration it must be expelled. Before final readings are taken, the liquid should remain red after boiling for two minutes. If this is not done, insufficient standard acid will be used.

Question 40.—Do you see any objection to dropping the carbonate into a measured quantity of acid?

Exercise 36.—Of the two liquids provided one is dilute nitric acid containing 1.5 grm. of nitrogen per litre, and the other a solution of potassium carbonate. Find the weight of potassium in 1 cu. cm. of the latter.

Directions.—1. Of 63.018 grm. (the mol) of HNO_3 14.01 grm. consist of nitrogen. From this find the weight of HNO_3 in 1 cu. cm. (See note on p. 152.)

2. Equation $\underbrace{2\,HNO_3}_{2 \times 63} + \underbrace{K_2CO_3}_{78.2} = 2\,KNO_3 + CO_2 + H_2O$ shows 39.1 grm. of K = 63 grm. HNO_3.

3. Acid in burette.

4. Use litmus for some titrations, and methyl orange for others, and compare the readings obtained. It is not necessary to expel the CO_2 when methyl orange is used. (See Ex. 13.)

Question 41.—4 grm. of caustic soda were dissolved up to 1 l. when it was found that 25 cu. cm. were neutralized by 22 cu. cm. of $\frac{N.}{10}$ HNO_3. Assuming that the alkali contained only sodium hydroxide and water, calculate the percentage of the latter in the sample.

Note the two methods of making the calculation:—

(i) Weight of HNO_3 used $= 0.0063 \times 22$ grm.
Equivalent weight of NaOH in 25 cu. cm.

$$= 0.0063 \times 22 \times \frac{40}{63} \text{ grm.}$$

Weight of NaOH in 1 l. $= 0.0063 \times 22 \times \frac{40}{63} \times \frac{1000}{25}$

$$= 3.52 \text{ grm.}$$

Weight of water in 4 grm. of caustic soda

$$= 0.48 \text{ grm.}$$

Per cent weight of water in sample

$$= \frac{0.48}{4.00} \times 100 = 12 \text{ per cent.}$$

(ii) Since $\frac{N.}{10}$ acid is used, the solution of NaOH is evidently $\frac{22}{25}$ of decinormal strength.

Now $\frac{N.}{10}$ NaOH contains 4 grm. per litre.

∴ our solution contains $4 \times \frac{22}{25}$ (or 3.52) grm. NaOH per litre.

Exercise 37.—With seminormal acid determine the percentage of sodium hydroxide in a sample of caustic soda, assuming that no carbonate is present.

Directions.—1. Assuming sample to be mainly NaOH, roughly calculate the weight necessary to make 250 cu. cm. of $\frac{N.}{2}$ solution. Although this weight will give a solution below $\frac{N.}{2}$ strength it will be sufficiently near to work with the acid.

2. Coarsely powder up some of the solid and transfer to a weighing-bottle with as little exposure to air as possible, then weigh the whole.

3. Transfer to the flask (in the way described in Ex. 35) the necessary quantity of the solid and weigh again.

4. Dissolve the solid in water, cool, fill up to the mark, and mix well.

5. Acid in burette.

6. Indicator: methyl orange or litmus; but should any carbonate be present boiling will be necessary with litmus.

Question 42. — In working Ex. 35 a student found 21.67 per cent of Na_2O in the sodium carbonate crystals. Calculate the number of molecules of water combined with Na_2CO_3.

Regard the crystals as made up of Na_2O, CO_2, and $x(H_2O)$.

21.6 parts by weight out of 100 consist of Na_2O,

15.38 parts $\left(\text{i.e. } 21.67 \times \frac{44}{62}\right)$,, ,, CO_2,

and the remainder—63 parts ,, ,, water.

$$\therefore \frac{\text{Total weight of water in crystals}}{\text{Total weight of } Na_2CO_3} = \frac{63}{37}.$$

$$\text{But } \frac{\text{Total weight of water in crystals}}{\text{Total weight of } Na_2CO_3} = \frac{x \text{ mol. of } H_2O}{1 \text{ formula weight of } Na_2CO_3} = \frac{x(18)}{106}.$$

$$\therefore \frac{x(18)}{106} = \frac{63}{37} \text{ and } x = 10.$$

Or, see method given in answer to Question 32 (*b*).

Question 43. —A sample of anhydrous sodium carbonate is known to contain a little sulphate. 2.65 grm. were dissolved and the solution made up to half a litre —25 cu. cm. of which required 18.5 cu. cm. of standard acid to neutralize it; whereas it was found that 25 cu. cm. of N. Na_2CO_3 required 18.75 cu. cm. of the same acid. Find (*a*) the percentage of pure Na_2CO_3 in the sample; (*b*) the weight of the impure salt which should have been taken to give strictly N. Na_2CO_3.

Exercise 38.—The sample of acid sodium sulphate is known to contain some sodium chloride. Find the weight of the salt which must be used to make a litre of $\frac{N.}{5}$ $NaHSO_4$.

Directions.—1. Find the weight which would be necessary were the salt pure. Take a quarter of this and dissolve up to 250 cu. cm.

2. Titrate with $\frac{N.}{10}$ alkali and find the exact weight of $NaHSO_4$ in that of the salt taken; then weight of the latter contains the necessary quantity of $NaHSO_4$.

Or, suppose it is found that 25 cu. cm. of solution require 40 cu. cm. $\frac{N.}{10}$ NaOH, or 20 cu. cm. of $\frac{N.}{5}$ solution of alkali. The salt contains only $\frac{20}{25}$ of its weight of $NaHSO_4$, from which the calculation can be made.

BACKWARD TITRATION METHOD

In previous exercises the estimations have been carried out by the "direct method", in which one standard solution only has been used in finding the strength of another. By using *two* standard solutions —one acid and one alkali—greater accuracy may be sometimes secured, and a larger number of estimations become possible. In estimating the strength of lime-water (Ex. 34) we could have added more than sufficient standard acid to neutralize the lime, and then found the excess by means of standard alkali. The difference between this and the quantity originally added represents the acid used in neutralizing the lime, from which the necessary calculation can be made as before.

The strength of many neutral salt solutions may be similarly determined. The metal may be precipitated by the addition of excess of standard sodium carbonate, the precipitate filtered off, when the excess of sodium carbonate can be found by standard acid. The difference, as before, represents the weight concerned in the reaction, from which the equivalent weight of the salt can be calculated.

Such methods are known as "residual methods" of analysis, or methods of "backward titration".

Exercise 39. — Determine the weight of barium chloride crystals dissolved in 1 l. of the bench reagent. The formula for the crystals is $BaCl_2, 2\,H_2O$.

Directions. — 1. To 25 cu. cm. of the reagent add a known volume of N. Na_2CO_3 in fair excess. Excess can be discovered by litmus paper.

2. Boil to complete precipitation; filter off the $BaCO_3$ and wash the vessel, filter-paper and precipitate three times with hot water, adding all washings to the filtrate, which should now contain all excess of Na_2CO_3.

3. Cool the filtrate and make it up with distilled water to a suitable volume (say 200 or 250 cu. cm.), and mix well.

4. Find the weight of Na_2CO_3 in filtrate, using $\frac{N.}{10}$ acid.

5. Weight of Na_2CO_3 used in precipitating the barium = weight originally taken less that found as excess. Let it be x grm.

Then weight of crystals dissolved in 25 cu. cm. $= x \times \frac{244 \cdot 3}{106}$

as shown by equation—

$$\underbrace{BaCl_2,\ 2\,H_2O}_{244 \cdot 3} + \underbrace{Na_2CO_3}_{106} = BaCO_3 + 2\,NaCl + 2\,H_2O.$$

6. Indicator: methyl orange.

N.B.—The calculation may be made in the usual way; but when solutions are used strictly N. or $\frac{\text{N.}}{10}$ it can be much shortened, as seen by the following example.

The bench reagent is about N. strength.

Suppose a student's records are—

Volume of $BaCl_2$ solution taken	25	cu. cm.
Volume of N. Na_2CO_3 taken ...	40	,,
Alkaline filtrate diluted to ...	200	,,

25 cu. cm. of diluted filtrate required 17.5 cu. cm. $\frac{\text{N.}}{10}$ acid.

The total excess of Na_2CO_3 will be that found in

$$\left(17.5 \text{ cu. cm.} \times \frac{1}{10} \times \frac{200}{25}\right),$$

or 14 cu. cm. of N. Na_2CO_3.

Volume of N. Na_2CO_3 used to precipitate the barium in 25 cu. cm. of solution

$$= (40 - 14) \text{ cu. cm.},$$

and weight of Na_2CO_3 so used

$$= 26 \times 0.106 \text{ grm.}$$

∴ weight of crystals dissolved in 1 l.

$$= 26 \times 0.106 \times \frac{244.3}{106} \times \frac{1000}{25} \text{ grm.}$$

Exercise 40.—A solution of hydrochloric acid provided is approximately normal. Find its exact value by means of calcite ($CaCO_3$).

Directions.—1. (The calcite should be quite transparent and colourless; otherwise you had better use pure dried precipitated calcium carbonate.) Grind a portion to fine powder and weigh out an exact quantity (about 1 grm.) from a weighing-bottle into a 250-cu.-cm. graduated flask.

2. Use 50 cu. cm. of the acid for solution. This should leave ample excess of acid.

3. Add water to the mark and mix well.

4. Find excess of acid with $\frac{N.}{10}$ alkali.

5. Indicator: methyl orange.

6. Equation—

$$\underbrace{CaCO_3}_{100.1} + \underbrace{2\,HCl}_{72.9} = CaCl_2 + CO_2 + H_2O.$$

Note.—If the acid is run into the alkali a precipitate of $Ca(OH)_2$ at first appears, but dissolves before the end-point is reached.

Exercise 41.—Find the concentration of calcium sulphate in your bench reagent by a volumetric method, and confirm your result gravimetrically.

Directions.—1. Precipitate the calcium in 100 cu. cm. of solution, using excess of N. Na_2CO_3. Complete precipitation by boiling for 3 min.

2. Filter into 250-cu.-cm. measuring-flask, washing precipitate, &c., well, and adding washings to the filtrate. (See Ex. 39.)

3. Cool, add water to mark, and mix well.

4. Find excess of Na_2CO_3 with suitable acid. What indicator will you use?

5. Equation to show the proportions of $CaSO_4$ and Na_2CO_3 which react:—

$$\underbrace{CaSO_4}_{136.1} + \underbrace{Na_2CO_3}_{106} = CaCO_3 + Na_2SO_4.$$

6. *Gravimetric Method.*—Evaporate a suitable quantity —50 to 100 cu. cm.—of the solution to dryness on a water bath, in a dish previously weighed. Then heat in an air oven kept at 120° to 140° till the weight after cooling in a desiccator is constant.

TWO INDICATORS USED IN ONE ESTIMATION

Exercise 42.—Titrate equal volumes of $\frac{N.}{10}$ Na_2CO_3 with $\frac{N.}{10}$ acid, using methyl orange alternately with phenolphthalein as indicators.

Directions.—1. Acid in burette.

2. Find the number of cubic centimetres of acid used when the colour change occurs with each indicator. What do you infer?

3. When the pink colour due to the phenolphthalein disappears add one drop of methyl orange, and continue adding the acid till neutralization is shown.

If the acid and alkali have been properly standardized, equal volumes should have been used when methyl orange shows the pink colour; but with phenolphthalein the solution should become colourless when *half* as much acid has been run in. The colour change of methyl orange occurs when acid and alkali are in the proportion shown by the equation—

$$Na_2CO_3 + 2\,HCl = 2\,NaCl + CO_2 + H_2O,$$

and that of phenolphthalein when in this proportion:—

$$Na_2CO_3 + HCl = NaHCO_3 + NaCl.$$

In other words, phenolphthalein is not sensitive to the bicarbonate. (See Exs. 13 and 14.)

It will also be noted that the presence of phenolphthalein does not interfere with the indications of methyl orange when no free alkali or normal carbonate is present. (See also notes on these indicators, pp. 139, 141.)

Exercise 43.—Estimate the percentage of sodium hydroxide and sodium carbonate present in the given sample of "soda ash", assuming that these are the only compounds present soluble in water.

Method I.—By the use of methyl orange and phenolphthalein.

Directions.—1. Assume sample to be wholly Na_2CO_3, and make 250 cu. cm. of about $\frac{N.}{3}$ or $\frac{N.}{2}$ strength. Use weighing-bottle. About what weight will you take? (See note on p. 152.)

2. Mix thoroughly, then allow the insoluble matter to subside before titrating.

3. N. acid will probably be found suitable to work with; if not, it must be diluted.

4. *Titrations.*—First, use phenolphthalein, which will show when *all* NaOH and *half* the Na_2CO_3 have been neutralized; then add methyl orange, which will show when the *remaining half* of Na_2CO_3 has been neutralized. The acid equivalent of this portion is thus directly read, and the total Na_2CO_3 can then be easily calculated.

If preferred, an entirely fresh titration may be made with methyl orange as indicator, when the *excess* of acid used over that used with the phenolphthalein will be the equivalent of half the Na_2CO_3 in the solution.

From the total quantity of acid used subtract that required by the Na_2CO_3—the remainder has been used by the NaOH present.

Method II.—By using barium chloride.

Directions.—1. Make solution as in Method I.

2. Find volume of N. acid necessary to neutralize both hydroxide and carbonate with methyl orange as indicator.

3. Precipitate all carbonate in 50 cu. cm. of the solution by adding excess of $BaCl_2$. (See Ex. 39.)

4. Filter off the $BaCO_3$, wash the precipitate, paper, and beaker well, adding washings to filtrate. If hot water is used, cool and make up to 100 or 200 cu. cm., and mix well. Or, the precipitate need not be filtered off. In this case make the solution up to 100 or 200 cu. cm. at once,

and after allowing the $BaCO_3$ to subside, neglect it, as it occupies very little volume.

5. Titrate the *clear* liquid with $\frac{N.}{10}$ acid. The quantity used will be equivalent to the NaOH in solution, and can thus be directly determined.

6. Weight of Na_2CO_3 will be the equivalent of the acid used in 2 less that used in 5.

It might appear that in the above exercise $Ba(OH)_2$ should also be precipitated by reaction with the NaOH thus: $BaCl_2 + 2NaOH = Ba(OH)_2 + 2NaCl$. But from such dilute solutions as we have used the small amount of $Ba(OH)_2$ formed remains dissolved. Solutions of $Ba(OH)_2$ can be made of one-fourth N. strength.

If soda ash contains free caustic soda, is its solution likely to contain bicarbonate as well?

ESTIMATION OF HARDNESS OF WATER

Exercise 44.—Determine the temporary hardness of spring water by Hehner's method, and express your result in "degrees of hardness".

Directions.—1. Assume temporary hardness as wholly due to $CaH_2(CO_3)_2$.

2. "Degrees of hardness" are given as the number of grammes of $CaCO_3$ found in 100,000 grm. of water. Assume 1 cu. cm. weighs 1 grm.

3. Titrate 100 cu. cm. at a time with $\frac{N.}{50}$ H_2SO_4 (50 cu. cm. $\frac{N.}{10}$ diluted to 250 cu. cm.), using methyl orange as indicator. From the weight of H_2SO_4 used, that of $CaCO_3$ in the water can be found.

4. Practically 1 cu. cm. $\frac{N.}{50}$ $H_2SO_4 = 0.001$ grm. H_2SO_4. Therefore each cubic centimetre used will indicate 0.001 grm. $CaCO_3$. If in the above exercise 13.5 cu. cm. $\frac{N.}{50}$ H_2SO_4 are

used, the presence of 0.0135 grm. $CaCO_3$ in 100 cu. cm. of the water is indicated; or 13.5 grm. in 100,000 grm. of water. The water will be said to possess 13.5 degrees of temporary hardness.

Question 44.—I add excess of sodium carbonate to some hard water known to contain both calcium carbonate and calcium sulphate in solution and boil. State what happens.

Question 45.—It was found that 0.53 grm. of sodium carbonate was necessary to react with the salts contained in a certain quantity of hard water. Assuming that the hardness was wholly due to calcium sulphate, (*a*) find the weight of this salt present in the water. (*b*) What quantity of water was used if it was found to possess 6.8 degrees of permanent hardness?

Exercise 45.—Determine the "permanent" hardness of the same sample of water, and express your result in "degrees of hardness".

Directions.—1. Assume all permanent hardness to be due to $CaSO_4$.

2. To 100 cu. cm. of the water add 20 cu. cm. $\frac{N.}{10}$ Na_2CO_3, and evaporate to dryness on a steam bath. (Platinum dish is preferable for this.)

3. Dissolve as much as possible of the residue in distilled water and filter. Wash all traces of Na_2CO_3 both from dish and filter paper, and add washings to filtrate.

4. Estimate the Na_2CO_3 in the filtrate with $\frac{N.}{50}$ H_2SO_4. This will be the excess Na_2CO_3 used.

5. Indicator: methyl orange.

6. Weight of Na_2Co_3 originally taken (i.e. 0.0053 × 20 grm.), less that found in excess, will have been used to precipitate the $CaSO_4$.

Note.—The carbonate precipitated will be $\frac{100}{106}$ of the weight of Na_2CO_3 used up; and it is usual to give as the number of degrees of permanent hardness the number of grammes of $CaCO_3$ which would be precipitated from 100,000 cu. cm. of the water, in the way stated instead of the number of grammes of $CaSO_4$ existing in this volume.

Question 46.—Some "soda water" containing nothing but carbon dioxide dissolved in water was passed into a known volume of standardized caustic soda, the latter being in excess. The solution then contained either caustic soda and normal carbonate, or the latter salt and acid carbonate. Can you suggest a volumetric method of estimating the carbon dioxide in 1 cu. cm. of the "soda water"?

ESTIMATION OF AMMONIUM SALTS

Suppose I wish to displace all the ammonia contained in 10 grm of ammonium nitrate; what weight (*a*) of sodium hydroxide, (*b*) of caustic soda containing 70 per cent of NaOH, will be theoretically required?

Equation $\underbrace{NH_4NO_3}_{80.1} + \underbrace{NaOH}_{40} = NaNO_3 + NH_3 + H_2O$

shows that practically 80 grm. of the salt require 40 grm. of NaOH; so that 10 grm. will require (*a*) 5 grm. NaOH, (*b*) $5 \times \frac{100}{70}$ or $7\frac{1}{7}$ grm. of the caustic soda.

Exercise 46.—Find the percentage of ammonia in some sal-ammoniac crystals (fairly pure).

Directions.—1. Use the "*indirect method*" since it is known that the sample is not very impure. Dissolve about a gramme in a small quantity of water contained in a small ordinary flask, and determine whether the solution is neutral. If found to be acid the amount of standard alkali necessary to neutralize it must be found and allowed for in your calculations.

2. Calculate the volume of N. NaOH necessary to expel the NH_3 from the weight of NH_4Cl taken. Equation—

$$\underbrace{NH_4Cl}_{53.5} + \underbrace{NaOH}_{40} = NaCl + NH_3 + H_2O$$

shows that $53\frac{1}{2}$ grm. require 40 grm. NaOH, or 1 grm. requires about $\frac{4}{5}$ grm. NaOH, which will be contained in 20 cu. cm. N. NaOH. About three times this volume, therefore, should be ample both to expel all NH_3 and leave sufficient excess when diluted to 250 cu. cm. to be accurately determined by $\frac{N.}{10}$ acid.

3. Add the N. NaOH—noting exact volume taken—to the solution of NH_4Cl, and boil till all NH_3 has been expelled. This may be determined by holding a damp litmus or turmeric paper in the steam.

4. Cool, transfer to a suitable measuring-flask, together with rinsings, add water to the mark, and mix well.

5. Determine excess of NaOH with suitable standard acid. The difference between this and that originally taken will be the equivalent of the NH_3 or NH_4Cl in the quantity of salt taken.

Note the following methods of calculation:—

A. Weight of crystals taken ... ... 1 grm.
Solution found to be neutral.
Quantity of N. NaOH added to expel NH_3
50 cu. cm. or ... ... 2 grm.
Residual alkali diluted to ... ... 250 cu. cm.
Volume taken at each titration ... 25 ,,
Average volume $\frac{N.}{10}$ H_2SO_4 required to
neutralize the alkali ... ... 31.3 ,,
Weight of H_2SO_4 used for each titration
(0.0049×31.3) grm.

Total H_2SO_4 used for excess of NaOH
$= (0.0049 \times 31.3 \times 10)$ grm. H_2SO_4.

Excess NaOH found

$$= \left(0.0049 \times 31.3 \times 10 \times \frac{40}{49}\right) = 1.252 \text{ grm. NaOH.}$$

Weight of NaOH used to expel all NH_3
$= (2 - 1.252)$ grm. $= 0.748$ grm.

Weight of NH_3 expelled $= 0.748 \times \frac{17}{40}$ grm.

Percentage of NH_3 in the crystals

$$= \frac{0.748 \times \frac{17}{40}}{1} \times 100 = 31.79 \text{ per cent.}$$

This being close to the theoretical value the crystals may be assumed to be pure.

B. This illustrates the saving of time when solutions accurately N. and $\frac{N.}{10}$ are used.

31.3 cu. cm. $\frac{N.}{10}$ acid were found $= \begin{cases} \text{25 cu. cm. diluted} \\ \text{NaOH.} \end{cases}$

$\therefore$ 313 cu. cm. $\frac{N.}{10}$ acid $= \begin{cases} \text{whole of residual NaOH in the} \\ \text{flask} = \text{31.3 cu. cm N. NaOH.} \end{cases}$

And since 50 cu. cm. N. NaOH were originally taken, 50 cu. cm. − 31.3 cu. cm. (i.e. 18.7 cu. cm.) N. NaOH were required to expel the NH_3,

And 18.7 cu. cm. N. NaOH = 0.04 × 18.7 grm.
= 0.748 grm.

Exercise 47.—Estimate the percentage weight of ammonia in a sample of commercial ammonium sulphate by the "direct" method.

Directions.—1. Fit up the apparatus shown in fig. 11.

A. Dropping-funnel containing strong solution of NaOH (5 to 10 grm. of solid dissolved in water). The funnel does not dip into the liquid in B.

B. Flask ($\frac{1}{4}$- to $\frac{1}{2}$-l. capacity) contains the weighed-out salt (1 to 2 grm.) dissolved in about 40 cu. cm. water; together with a piece of granulated zinc to prevent boiling by bumping.

C contains small pieces of clean broken glass. 100 cu. cm. of N. acid are carefully poured through it into flask D. The moistened glass will now trap any NH_3 which escapes combination with the main bulk of acid in D.

E. The delivery-tube, should be fairly wide and cut off obliquely at *both* ends, one of which is shown enlarged at F. Note that it *almost* touches the surface of the acid in D. If this is properly cut and carefully adjusted, the acid cannot regurgitate into B, and there will be less chance of NaOH being carried forward in the steam from B to D. The tube is conveniently made in two parts joined by a rubber connection.

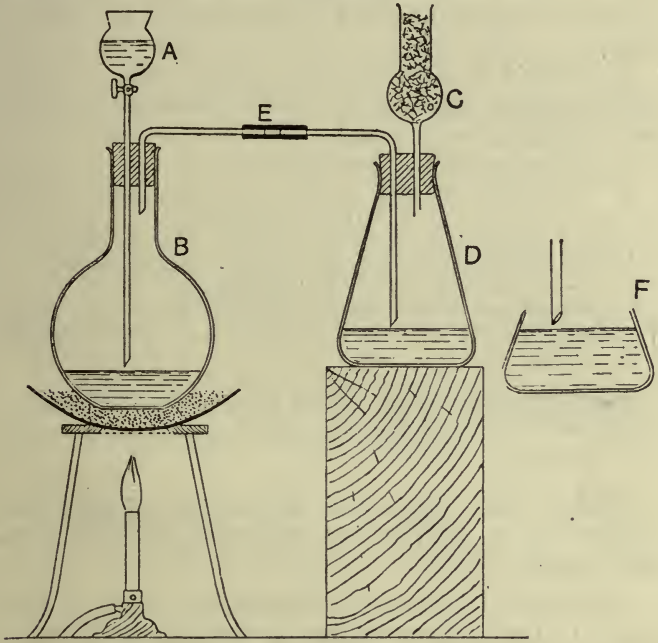

Fig. 11

The corks used should be of rubber, and all fittings must be air-tight.

2. Allow the NaOH in A to flow into B, close the stopcock, and boil *gently* until half to two-thirds of the water

in B has passed over. Rapid boiling tends to drive some of the alkali over into D and thus vitiates the result.

During this process the delivery-tube passing into D will probably require some readjustment.

3. When all NH_3 has been driven over into D, with a jet of distilled water thoroughly wash down all acid from the pieces of glass in C and from the end of the delivery-tube.

4. The acid in D may be now transferred to a suitable graduated flask, made up to a known volume, and titrated with suitable standard alkali.

5. Indicator: methyl orange.

6. The weight of acid which has been neutralized will be the equivalent of the NH_3 contained in the salt taken.

Notes.—(i) The above is known as the "direct method", and may be used in estimating any ammonium salt.

(ii) Ammonium sulphate is a valuable by-product in the manufacture of coal-gas. It is useful as a manure on account of its nitrogen.

Question 47.—What weight of nitrogen is there in a kilogram of the sample of ammonium sulphate you have just estimated?

Exercise 48.—Find the proportion of each salt present in a mixture of chlorides of ammonium and sodium.

Directions.—1. Determine the weight of NH_3 in about 2 grm. of the mixture by either of the foregoing methods. If this is x grm., the weight of NH_4Cl present will be $\frac{535}{170}x$ grm.

2. Find the weight of NaCl by difference.

Note.—This may also be done by estimating the percentage of chlorine in the mixture. See Questions 76, *et seq.*

Exercise 49.—A solution contains both caustic soda and free ammonia. Find the weight of each dissolved in 1 l.

Directions.—1. Find the weight of acid required to neutralize the total alkali in a given volume.

2. Repeat (1) after boiling off the ammonia, when the weight of NaOH can be found.

3. The weight of NH_3 can be found from the difference in the weights of acid used in (1) and (2).

THE ESTIMATION OF ORGANIC ACIDS

In comparison with mineral acids these are "weak", and it will be well to examine the behaviour of some of their salts containing strong and weak bases with different indicators.

Exercise 50.—Find the effect of dilute solutions of acetates, &c., of such bases as sodium, ammonium, lead, &c., upon litmus, methyl orange, and phenolphthalein.

Exercise 51.—Assuming the acidity of the vinegar provided to be wholly due to acetic acid, find its percentage weight in the sample.

Directions.—1. Use $\frac{N.}{2}$ NaOH, free from Na_2CO_3.

2. Equation

$$CH_3.COOH + NaOH = CH_3.COONa + H_2O.$$

3. Indicator: phenolphthalein. Why?

The colour change can be better followed by dropping the vinegar into the alkali. Should the vinegar be so dark coloured as to obscure the end-point, a strip of paper dipped in the indicator may be used externally.

4. Do not assume that 1 cu. cm. of the vinegar weighs 1 grm. Find the weight of a definite volume.

5. Percentage required $= \dfrac{\text{weight of acid}}{\text{weight of vinegar}} \times 100.$

The *equivalent of an organic acid* is the weight required to neutralize one equivalent of alkali.

In carrying out this determination the most reliable indicator is phenolphthalein. But since caustic soda or potash is apt to contain carbonate, and the pink colour due to this indicator disappears when only half the carbonate has been decomposed, standard baryta is preferred, as its clear solution can contain no carbonate, and any formed by reaction with carbon dioxide can be immediately detected.

Exercise 52.—Prepare some decinormal barium hydroxide.

Directions.—1. Introduce 4 to 5 grm. of the finely powdered crystallized hydroxide into about 200 cu. cm. of distilled water contained in a flask. Cork, and allow to stand for a couple of days, shaking up occasionally. The saturated solution produced will be about $\frac{N.}{5}$.

2. Decant the clear liquid into a clean flask fitted with rubber cork.

3. Find its exact strength with $\frac{N.}{10}$ HCl. Indicator: phenolphthalein.

$$\text{Equation } \underbrace{Ba(OH)_2}_{171.4} + \underbrace{2\,HCl}_{72.9} = BaCl_2 + 2\,H_2O.$$

4. Dilute to $\frac{N.}{10}$ strength with freshly boiled and cooled distilled water.

5. *Test your result gravimetrically.*

Measure out 25 cu. cm. into a weighed dish, and add dilute H_2SO_4 until slightly acid. Evaporate to dryness on a water bath, then ignite at dull red heat for five to ten minutes over a Bunsen flame. Cool in exsiccator and weigh. The weight of $Ba(OH)_2$ in the solution taken was $\frac{171.4}{233.4}$ that of the sulphate formed.

Note.—The stock bottle for baryta water should be fitted with rubber stopper and "calcium chloride tube" containing dry soda-lime.

Exercise 53.—Make some one per cent (approx.) solution of tartaric acid, and determine the equivalent of the acid.

Directions.—1. Dissolve up about 2 grm. of crystals, accurately weighed, to make 200 cu. cm. of solution.

2. Titrate with $\frac{N.}{10}$ $Ba(OH)_2$. Indicator: phenolphthalein.

3. Since barium has diad valency, the equivalent of the acid will be that weight in grammes which neutralizes half the gramme formula weight (85.7) of $Ba(OH)_2$. (See notes, p. 152.)

Basicity and Molecular Weight of Organic Acids.—When a definite weight of some particular alkali is neutralized by acid, a salt is produced which may often be easily crystallized out and identified. Some acids invariably yield the same salt no matter in what proportions acid and alkali are mixed, and the reagent in excess remains mixed with the salt. There are others which can be induced to form more than one distinct salt when the acid is in excess of that necessary to form the normal salt. In every such case, however, it is found that the quantity of acid required to form "acid salts" bears a simple ratio to that necessary for the production of the normal salt, provided the same weight of alkali is used. Acids may thus be classified as monobasic, dibasic, &c., according to the number of distinct salts each can form with some particular alkali. In the case of a dibasic acid, the quantity found necessary to form the acid salt is just double that required to form the normal salt.

The number of salts which an organic acid is capable of forming with an alkali thus furnishes a clue to its molecular weight. Since monobasic acids can form one salt only with an alkali, it is assumed that their molecules contain only one hydrogen atom replaceable by metal; and consequently that weight of the acid (in grammes) which can be neutralized by 40 grm. of NaOH is assumed to be its molecular weight. The molecular weight of a monobasic acid is thus equal to its equivalent. In the case of a dibasic acid, since the acid salts derived from it must contain at least one atom of sodium (or other monad radical), and that proportionately twice as much sodium hydroxide is required to produce the normal salt, it follows that the acid contains at least two replaceable hydrogen atoms, and its gramme molecular weight may be assumed to be that neutralized by 80 grm. of NaOH. In other words, it is assumed to be twice the equivalent.

Speaking generally then, the molecular weight of an organic acid = its equivalent × basicity. (For other methods of determining basicity see works on Physical Chemistry.)

Question 48.—The formula given to tartaric acid may be written $C_4H_6O_6$. From its equivalent (found in Ex. 53) what would you conclude its basicity to be?

Exercise 54.—Oxalic acid whose formula may be represented as $H_2C_2O_4$ crystallizes with two molecules of water. Find its basicity.

Directions.—1. 3 grm. of crystals dissolved up to 250 cu. cm. will work with $\frac{\text{N.}}{10}$ alkali.

2. Indicator: phenolphthalein.

3. Basicity $= \frac{\text{molecular weight}}{\text{equivalent}}$.

(See notes, p. 152.)

Note on the term "Equivalent".—It is interesting to remember

CALIFORNIA COLLEGE of PHARMACY

that the idea of equivalence was first suggested by the discovery in the latter part of the eighteenth century, that different weights of various bases were necessary to neutralize one and the same weight of acid. These different weights were said to be "equivalent" in neutralizing power. Further research showed a similar relationship between elements. Wollaston used the term for the proportional weights in which elements combine, and fixed that of hydrogen as unity, because its proportional weight in a compound was found to be invariably less than that of any other element.

Question 49.—The formula for acetic acid is $H_4C_2O_2$, and it is found that 2 grm. of sodium hydroxide neutralize 3 grm. of the acid. (*a*) Find what weight of the acid should be contained in a litre of normal strength. (*b*) What inference do you draw as to the basicity of the acid?

Question 50.—On titrating an aqueous solution of a dibasic organic acid containing 1 grm. in 250 cu. cm. with $\frac{N.}{10}$ baryta water, it was found that 25 cu. cm. of the acid solution required 22.2 cu. cm. of $\frac{N.}{10}$ $Ba(OH)_2$ to neutralize it. What is the formula weight of the acid?

Question 51.—Two solutions A and B of the same acid were prepared, A containing 8 grm. and B 14 grm. B was partly neutralized by the addition of 8 grm. of alkali, and each solution was made up to 1 l. On titrating the acid solutions with unstandardized caustic soda it was found that 20 cu. cm. of the latter neutralized 10 cu. cm. of A and 40 cu. cm. of B. Find the ratio between the weights of acid and alkali necessary to neutralize each other.

Question 52.—In another case it was found that B was alkaline, and that 5 cu. cm. of A were necessary to neutralize 25 cu. cm. of B. What is the ratio in this case?

Question 53.—Some solutions of caustic potash and baryta water were titrated against acid, when it was found that 50 cu. cm. of baryta water and 40 cu. cm. of the potash were necessary to neutralize equal volumes of the acid. Compare the number of atoms of metal present in equal volumes of the solutions.

CHAPTER VII

Methods depending on Direct Oxidation and Reduction

The chief compounds used in volumetric estimations involving direct oxidation are potassium permanganate and potassium dichromate, both of which are readily reduced to other substances. In each case the change is sharp and easily detected.

Potassium Permanganate ($KMnO_4$).—The reaction between this compound and the reducing agent hydrogen sulphide may here be recalled. The odour of the one and the purple colour of the other disappeared together, and it was evident that new substances were formed. The addition of dilute sulphuric acid prevented the formation of the dark precipitate of manganese hydroxide, and allowed the colour change to be readily followed. A standard solution of permanganate can be used in the estimation of several substances which tend to pass into a more highly oxidized condition; but its commonest use is for estimating ferrous iron.

Exercise 55.—Find the effect of dropping some dilute permanganate solution into ferrous and ferric solutions separately with and without the previous addition of dilute sulphuric acid; also into dilute and concentrated sulphuric acid alone.

Directions.—1. Use $FeSO_4$ and $FeCl_3$.

2. Add the $KMnO_4$ till the solutions become permanently coloured.

There appears to be no reaction between permanganate and ferric solutions, whether acid is present or not, as the purple colour is retained from the first drop. This is not so with ferrous solutions, as the colour is instantly destroyed and does not appear until a certain quantity of the permanganate has been added, when the appearance resembles that in the ferric solution. We may therefore assume that at this point there is no ferrous iron remaining. Dilute sulphuric acid has no apparent action on permanganate, but it prevents precipitation of oxides of manganese and iron in the above reaction, and allows the colour change to be clearly seen. Ferrous sulphate and permanganate may be supposed initially to break up thus—

$$\begin{aligned}&10\,FeO,\ SO_3 + K_2O,\ Mn_2O_7\\&\qquad = 5\,Fe_2O_3 + 2\,MnO + K_2O + 10\,SO_3.\end{aligned}$$

Ten equivalents only of SO_3 are supplied by the ferrous sulphate, whereas eighteen are required to convert the whole of the oxides to soluble sulphates. Eight equivalents must therefore be supplied by added sulphuric acid. A great excess of this acid must be avoided, as it is capable of reducing the permanganate to green manganate. Strong sulphuric acid decomposes solid permanganate on heating—sometimes with violence, when oxygen is liberated:—

$$\begin{aligned}&4\,KMnO_4 + 8\,H_2SO_4\\&\qquad = 4\,KHSO_4 + 4\,MnSO_4 + 6\,H_2O + 5\,O_2.\end{aligned}$$

The reaction between ferrous sulphate and potassium permanganate in the presence of dilute sulphuric acid may now be written—

$$\begin{aligned}&\underbrace{2\,KMnO_4}_{316.1} + \underbrace{10\,FeSO_4}_{558.4\,(Fe'')} + 8\,H_2SO_4\\&\qquad = 5\,Fe_2(SO_4)_3 + K_2SO_4 + 2\,MnSO_4 + 8\,H_2O;\end{aligned}$$

316.1 grm. of the permanganate being necessary to supply the oxygen required by 558.4 grm. of ferrous iron for its conversion to the ferric condition. It will be evident, therefore, that when the strength of a solution of either salt is known, that of the other can be easily determined. It need hardly be pointed out that in the estimation of the *total* iron in a solution by this method, care must be taken to have it wholly in the ferrous condition. Now it might appear that any standard solution of permanganate can be easily prepared by dissolving the required weight of solid up to the proper volume. Unfortunately, however, the salt is not very soluble (it requires fifteen times its weight of water for complete solution); and, in addition, the solid being apt to suffer slight decomposition, the formula $KMnO_4$ cannot be relied upon as representing its exact composition. It is usual to prepare a solution somewhat above decinormal strength, determine its exact value by titration against some specially prepared ferrous solution, then dilute it to the required standard. The ferrous solution may be made by dissolving in sulphuric acid a known weight of the purest iron wire obtainable, taking proper precautions to prevent oxidation by air. The excess of acid present does not matter. Or, a known weight of pure ferrous salt may be dissolved up to a given volume with similar precautions. Ferrous ammonium sulphate is usually considered the best for this purpose, as in the presence of the ammonium salt the ferrous sulphate does not oxidize so readily. (See also p. 28.)

The chief points to be remembered in using permanganate are—

1. The salt, whether solid or in solution, is apt to suffer some decomposition on keeping. Dr. Friend

says that, unless pure, a solution is apt to alter in value in a few days.

2. The solid does not dissolve very readily; and undissolved particles may easily escape detection in the highly coloured liquid.

3. It is decomposed by rubber, paper, and other organic matter, as well as by ordinary reducing agents. Filtering a standard solution through paper, or using it in an ordinary Mohr's burette, therefore reduces its strength.

4. It reacts with hydrochloric acid, and liberates chlorine, unless the acid is present in very small quantity, or unless manganous or ammonium sulphate is present as well. About 0.5 grm. added to 25 cu. cm. of ferrous solution is found to be sufficient to prevent this reaction.

$$K_2O, Mn_2O_7 + 16\,HCl = 2\,MnCl_2 + 2\,KCl + 5\,Cl_2 + 8\,H_2O.$$

Exercise 56.—Make solutions of ferrous sulphate and ferrous ammonium sulphate, and test for ferric iron.

Direction.—Use potassium ferrocyanide ($K_4FeC_6N_6$) and ammonium sulphocyanide (NH_4SCN).

Exercise 57.—Prepare about 20 grm. of "Mohr's salt" (ferrous ammonium sulphate crystals) in a finely crystalline condition.

Directions.—1. Dissolve formular proportions of the purest crystals of ferrous sulphate and ammonium sulphate separately in the smallest quantity of moderately hot distilled water recently boiled, and add a few drops of dilute H_2SO_4. Formula weight of $FeSO_4, 7\,H_2O = 278$; that of $(NH_4)_2SO_4 = 132.2$. $\frac{1}{20}$ of these weights in grm. should yield 18 to 20 grm. of the required crystals.

2. Mix the solutions and cool whilst constantly agitating, so as to produce small crystals.

3. After standing about an hour, filter and dry the crystals thoroughly by pressure between filter paper, then expose them to air until they do not clog together.

4. Preserve in a stoppered bottle.

5. Formula: $Fe(NH_4)_2(SO_4)_2, 6\,H_2O$.

Question 54.—What weight of iron is contained in a formula weight of Mohr's salt? What proportion of the salt consists of iron? What weight of the crystals should be dissolved up to 250 cu. cm. to make a solution equivalent to $\frac{N.}{10}$ $KMnO_4$?

316.06 grm. $KMnO_4$ lose 80 grm. of oxygen in oxidizing 558.4 grm. of ferrous iron. ∴ 1 cu. cm. $\frac{N.}{10}$ solution = 0.00316 grm. $KMnO_4$, and the iron ammonium solution must contain 0.00558 grm. Fe'' which is contained in 0.004102 grm. of the crystals. 250 cu. cm. of $\frac{N.}{10}$ ferrous ammonium sulphate will therefore require 10.2 grm. of crystals.

Exercise 58.—Make a litre of $\frac{N.}{10}$ permanganate solution, standardizing it with your own ferrous ammonium sulphate.

Directions.—1. Grind the $KMnO_4$ to a fine powder to ensure quick solution, and dissolve 3.5 grm. up to a litre.

N.B.—Be careful that the solution is complete before titrating. To ascertain this, allow the liquid to stand a few minutes, and decant it into another vessel. Do not filter through paper.

2. Use recently boiled distilled water to dissolve the $FeAm_2SO_4, 6\,H_2O$. Take care that it is quite cold before making up to the mark.

3. $KMnO_4$ in burette with glass tap.

4. Add a few cubic centimetres of dilute H_2SO_4 to each portion of ferrous solution titrated. A brown precipitate shows insufficiency of acid.

5. Drop in the $KMnO_4$ till a permanent faint-pink colour is obtained.

6. Read to the surface of the $KMnO_4$.

7. If you have made your ferrous solution exactly $\frac{N.}{10}$, 25 cu. cm. should require less than 25 cu. cm. of the $KMnO_4$ solution.

8. *To make the necessary dilution*—

Suppose 25 cu. cm. $\frac{N.}{10}$ Fe″ solution = 22.5 cu. cm. $KMnO_4$. Evidently 22.5 cu. cm. contain as much $KMnO_4$ as 25 cu. cm. $\frac{N.}{10}$ $KMnO_4$. So 22.5 cu. cm. must be made up to 25 cu. cm., or 900 cu. cm. to 1 l.

Exercise 59.—With dilute sulphuric acid and iron wire whose percentage purity is known, make a solution of ferrous salt, and with it check the result obtained in the last exercise.

Directions.—1. Make 100 or 200 cu. cm. This solution easily oxidizes, and is made as required.

2. Accurately weigh sufficient wire cut into pieces. [Piano wire or fine binding wire may be assumed to contain 99.6 per cent Fe. For 100 cu. cm. $\frac{N.}{10}$ ferrous solution, 100×0.00558 grm. will be required; i.e. about 0.5 grm. will do very well.]

3. Calculate the weight of pure iron in the quantity of wire taken.

4. *To prevent the formation of ferric compound during solution* (by contact with air). Fit the flask with cork and exit tube, &c., as shown either in A or B (fig. 12). One-third fill it with dilute H_2SO_4, and drop in 1 or 2 grm. of pure $NaHCO_3$, and then the iron wire. When the evolution of

CO_2 slackens replace cork, &c. The expelled gas will drive all air out of the flask. Solution will be quickened by gently heating.

In A the expelled hydrogen is bubbled through freshly boiled water contained in the beaker. When solution is complete, some of this water may be allowed to pass backwards into the flask. B is a Bunsen valve, i.e. a piece of rubber tubing with a clean slit cut lengthwise about half an inch long. It is slipped over the projecting tube, while the free end is stopped with the glass rod. This arrangement allows hydrogen and steam to escape, while it prevents air from entering, since the edges of the slit close up.

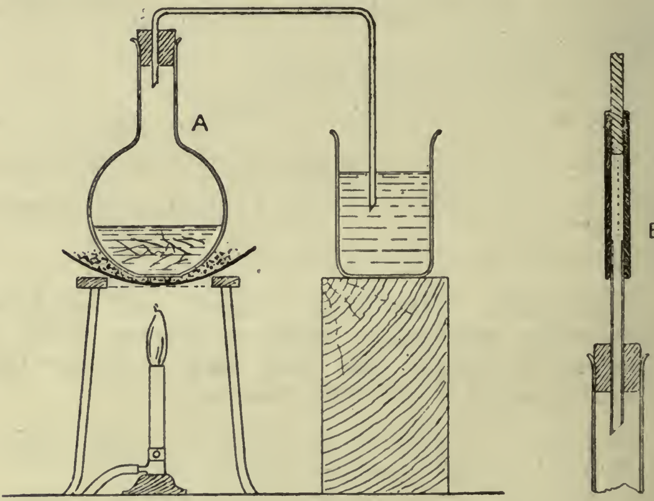

Fig. 12

5. When the iron has dissolved cool quickly, and make up to the mark with distilled water recently boiled and cooled. The carbon particles may be neglected.

Note.—If carefully prepared, this solution should give a more reliable result than the ferrous ammonium solution.

Exercise 60.—Prepare some pure crystals of oxalic acid from cane sugar.

Directions.—1. Do this in a fume closet.

2. In a porcelain dish heat 70 cu. cm. of strong HNO_3 to about 100° C.; then having removed it from the flame, add 15 grm. of cane sugar.

3. After the reaction has ceased, evaporate to a quarter its bulk, and set aside till cold.

4. Separate the crystals, and dry them on filter paper.

5. Redissolve them in the smallest possible quantity of hot water, and allow the crystals to form again. This may be repeated.

6. Dry the crystals thoroughly, and keep in a stoppered bottle.

Question 55.—Oxalic acid is dibasic, and its crystals are represented by the formula $H_2C_2O_4,\ 2\,H_2O$. What weight should be taken to make 1 l. of $\frac{N.}{10}$ acid?

Exercise 61.—Test the purity of your crystals by titration against standard alkali.

Directions.—1. Weigh out sufficient crystals to make 50 cu. cm. of acid presumably $\frac{N.}{10}$. This will be sufficient for this and the next exercise.

2. Use $\frac{N.}{10}$ NaOH and phenolphthalein.

3. 80 grm. NaOH = 126 grm. of crystals—

$$\underbrace{H_2C_2O_4,\ 2\,H_2O}_{126} + \underbrace{2\,NaOH}_{80} = Na_2C_2O_4 + 4\,H_2O.$$

Note.—Decinormal oxalic acid is not stable, and should be prepared as required. Stock solution should be of N. strength.

Exercise 62.—Find the weight of oxalic acid necessary to reduce 3·16 grm. of potassium permanganate.

Directions.—1. $\frac{N.}{10}$ $KMnO_4$ in burette.

2. Use the oxalic solution prepared in the last exercise. To each portion add a little dilute H_2SO_4 or HCl. Half the titrations might be made with each acid, noting any difference in the results.

3. Before titrating, heat each portion to 60°, as the reaction takes place very slowly in the cold.

4. Equation expressing the reaction:—

$$\underbrace{2\,KMnO_4}_{316} + \underbrace{5\,(H_2C_2O_4,\ 2\,H_2O)}_{630} + 3\,H_2SO_4$$
$$= K_2SO_4 + 2\,MnSO_4 + 10\,CO_2 + 18\,H_2O.$$

N.B.—Accurate work in the last exercise will show that the reaction is complete when equal volumes of $\frac{N.}{10}$ $KMnO_4$ and $\frac{N.}{10}$ $H_2C_2O_4$ are mixed—a result which would be expected in a reaction between the acid and an alkali. Here, however, we are not neutralizing the acid, but breaking up its molecules by the oxidizing power of the permanganate. Oxalic-acid solution, therefore, made of standard strength, either for its acid or reducing properties, contains the same proportion of the compound.

Question 56.—1 l. of a certain solution contains 0.549 grm. of manganese as potassium permanganate. 20 cu. cm. of a ferrous solution require 24.5 cu. cm. of the permanganate to transform all ferrous iron to ferric. (*a*) Find the weight of ferrous iron in 1 l. of the solution. (*b*) Express the strength of the permanganate in the usual way, viz.:—

1 cu. cm. = x grm. $KMnO_4$
1 cu. cm. = x grm. oxygen
1 cu. cm. = x grm. Fe''.

Question 57.—How many formula weights of oxalic acid have the same reducing effect on permanganate as one of ferrous sulphate?

Exercise 63.—Find the number of molecules of combined water in ferrous sulphate crystals.

Directions.—1. Use recently boiled and cooled distilled water to make the solution, to which a few drops of concentrated H_2SO_4 have been added to hinder oxidation.

2. Pick out clear green crystals, and grind up before weighing out.

3. About 4 grm. to 250 cu. cm. will work with $\frac{N.}{10}$ $KMnO_4$.

4. Find the weight of $FeSO_4$ in that of crystals taken; the difference will represent the weight of water combined with it.

5. Calculate the weight of water combined with a gramme formula weight of $FeSO_4$. The weight found divided by the gramme molecular weight of water will give the required answer.

Exercise 64.—The solution of iron salt was originally ferrous. (*a*) **Find whether any ferrous iron is still present.** (*b*) **Reduce all ferric iron to the ferrous condition.** (*c*) **Find the weight of each kind of iron in 1 l. of the solution.**

Directions.—1. *To test for ferrous salt* use potassium ferricyanide ($K_3FeC_6N_6$), which gives Turnbull's blue (resembling Prussian blue)—

$$2\,K_3FeCy_6 + 3\,FeSO_4 = \underset{\text{(Turnbull's blue)}}{Fe''_3(FeCy_6)_2} + 3\,K_2SO_4.$$

Potassium ferricyanide gives no blue colour with ferric salt.

2. *To test for ferric salt* when reduction is supposed to be complete, use potassium (or ammonium) sulphocyanate. This reagent yields a blood-red solution with ferric compounds, due to a double salt represented by the formula $Fe'''(CNS)_3, 9\,KCNS, 4\,H_2O$. In the solid state it resembles potassium permanganate.

$$12\,KCNS + FeCl_3 + 4\,H_2O$$
$$= Fe'''(CNS)_3, 9\,KCNS, 4\,H_2O + 3\,KCl.$$

[Potassium ferrocyanide is not so suitable, as it yields

Prussian blue, $Fe_4(FeCy_6)_3$, with ferric salts, and with ferrous salts a white precipitate of potassium ferrous ferrocyanide, $K_2Fe''(FeCy_6)$, which at once turns blue by reaction with dissolved oxygen or with that free in the air.]

3. *Reduction.* Transfer a definite volume of the solution, say 25 cu. cm., to a flask, and add a few thin pieces of zinc free from iron, together with sufficient dilute H_2SO_4 to dissolve them. Prevent access of air by one of the methods given in Ex. 59. Gentle heat may be applied. The reduction is chiefly due to the nascent hydrogen. When the solution appears colourless, remove a drop on a clean glass rod, and test for ferric iron by mixing it with a drop of solution of KCNS placed on a white tile. A red colour indicates that the process of reduction must be carried further. It may be considered complete when only a faint tint appears, as this may be due to the exposure of the ferrous liquid to the air.

4. *Titration.* . Before titrating, note the following points:—

(i) All zinc must have been dissolved; if this has not been effected, undissolved pieces must be removed, or they will reduce some of the $KMnO_4$ run in, and of course introduce error. The $ZnSO_4$ does not interfere.

(ii) Ascertain whether the solution contains chloride. If more than a trace is present, add a little $MnSO_4$ or $(NH_4)_2SO_4$. 0.5 grm. to each 25 cu. cm. will be ample.

(iii) Sufficient H_2SO_4 must be present, yet not in so concentrated a form as to reduce the $KMnO_4$. Use $\frac{N.}{10}$ $KMnO_4$ and find the total iron present. Original ferrous iron must be determined by a separate titration. The difference between the two results represents the ferric iron—

$$316 \text{ grm. } KMnO_4 = 558 \text{ grm. } Fe''.$$

Exercise 65.—Find the effect of metallic zinc in the form of dust on solutions of ferric salt and potassium permanganate.

Directions.—1. Shake up a little zinc dust in dilute $FeCl_3$ solution. The addition of half a dozen drops of dilute H_2SO_4 will remove any coating of ZnO on the particles. Continue shaking till the liquid appears colourless on standing.

2. When colourless, test for ferric iron with KCNS. ("Drop test", see Ex. 64.) If the reduction is incomplete, continue the treatment with zinc dust.

3. Repeat 1, using very dilute $KMnO_4$ instead of $FeCl_3$.

[The above is Carnegie's method of reducing ferric salts, and though not so perfect as that previously given, is much speedier.]

Exercise 66.—Find the percentage of iron in iron alum by means of standard permanganate.

Directions.—1. Solution of 2 to 3 grm. of the salt in 250 cu. cm. will work with $\frac{N.}{10}$ $KMnO_4$.

2. Test for ferric iron, and reduce all present.

3. Reduce two or three separate quantities of 25 cu. cm. with nascent hydrogen (see Ex. 64), and one quantity of about 75 cu. cm. with zinc dust, in order to be able to compare the two methods.

4. Since zinc reduces $KMnO_4$, the residual dust must be removed. Ordinary filtration would allow considerable reoxidation of the iron. A "reversed filter" is less objectionable. Fig. 13 shows this arrangement.

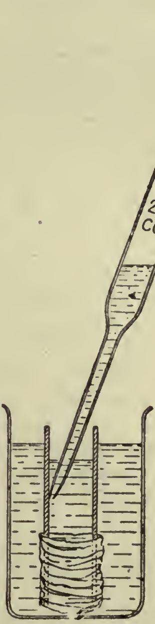

Fig. 13

A double piece of filter paper is tied tightly round the end of a glass tube wide enough to take the pipette easily. When stood vertically in the flask (or narrow beaker), a clear liquid filters through, and may be withdrawn in the usual way.

Exercise 67.—The solution contains ferrous sulphate and oxalic acid mixed in proportion to their formula weights. Find the weight of crystals of each used in making 1 l. of the solution.

Directions.—1. Since we have to find the quantity of ferrous compound present, reduction is unnecessary.

2. Acidify each portion withdrawn for titration with dilute H_2SO_4, warm to 60°, and titrate with $\frac{N.}{10}$ alkali.

3. The equations—

$$\begin{aligned} 4\,FeSO_4 + 2\,H_2SO_4 + O_2 &= 2\,Fe_2(SO_4)_3 + 2\,H_2O \\ 2\,H_2C_2O_4 \qquad\qquad + O_2 &= 4\,CO_2 + 2\,H_2O \end{aligned}$$

show that each formula weight of oxalic acid uses twice as much oxygen, and therefore twice as much $KMnO_4$ as a formula weight of $FeSO_4$. Consequently, one-third of the $KMnO_4$ used will be the equivalent of the ferrous salt, and the remaining $KMnO_4$ that of the oxalic acid.

Ferrous sulphate crystals are represented by $FeSO_4$, $7\,H_2O$, and oxalic-acid crystals by $H_2C_2O_4$, $2\,H_2O$.

Question 58.—How would you have determined the quantity of each present, if *equal weights* of the crystals had been dissolved?

Formula weight of $FeSO_4$, $7\,H_2O$ = 278.
Formula weight of $H_2C_2O_4$, $2\,H_2O$ = 126.

From equations in Ex. 67 it is evident that 63 grm. of oxalic crystals require as much permanganate as 278 grm. of the ferrous crystals. If x grm. of $KMnO_4$ is used by the oxalic acid, $\frac{278x}{63}$ grm. will be required by the ferrous crystals.

Then $\frac{278x}{63} + x =$ total $KMnO_4$ (in grammes) used.

Question 59.—1 l. of ferrous sulphate solution is made by dissolving 5 grm. of ferric oxide in dilute sulphuric acid, reducing to the ferrous state, and adding the necessary volume of water. 25 cu. cm. are found to require 35 cu. cm. of a permanganate solution to reoxidize the ferrous salt. (*a*) Find the strength of the potassium permanganate. (*b*) Calculate the volume of water which must be added to or withdrawn from 750 cu. cm. of the permanganate to make it $\frac{N.}{20}$.

Question 60.—What weight of oxygen available for oxidizing purposes can be obtained from 1 l. of hydrogen peroxide solution containing 40 grm. of peroxide?

Exercise 68.—Find the percentage weight of hydrogen peroxide contained in the laboratory solution by means of $\frac{N.}{10}$ $KMnO_4$.

Directions.—1. The two highly oxidized compounds mutually decompose each other. Equation—

$$\underbrace{5\,H_2O_2}_{170.1} + \underbrace{2\,KMnO_4}_{316} + 3\,H_2SO_4 = K_2SO_4 + 2\,MnSO_4 + 5\,O_2 + 8\,H_2O,$$

shows that 316 grm. $KMnO_4$ = 170.1 grm. H_2O_2.

2. Into a weighed 100-cu.-cm. measuring-flask pour about 10 cu. cm. of the solution, and find its weight.

3. Test the original H_2O_2 solution for HCl. If present in any quantity add a little $MnSO_4$ to the weighed peroxide.

4. Make up to the mark with distilled water, and mix well.

5. To each portion titrated add about half its volume of dilute H_2SO_4.

Note.—The presence of organic matter will interfere with the results. A more reliable method of estimating the peroxide is given in Ex. 85.

Question 61.—When barium peroxide is acted upon by acid—preferably phosphoric—in ice water, the barium salt is precipitated and hydrogen peroxide passes into solution. (*a*) What volume of $\frac{N.}{8}$ permanganate solution will be required to decompose the hydrogen peroxide theoretically produced from 10 grm. of the pure barium compound? (*b*) What volume would the oxygen occupy at S.T.P.?

Potassium Dichromate ($K_2Cr_2O_7$).—The use of this reagent for oxidizing purposes was illustrated in Exs. 9 and 18. To detect the end-point of its reaction with reducing agents, it was found necessary to use an external indicator, as the green chromium salt formed prevents detection of excess dichromate. But for this one disadvantage potassium dichromate is preferable to permanganate, for the following reasons:—

(i) The solid is less liable to decomposition, and may be assumed to be in accord with its formula.

(ii) Its solution is less likely to deteriorate.

(iii) It does not react with rubber, and consequently may be used in an ordinary Mohr's burette.

(iv) Its reactions are not interfered with by hydrochloric acid.

When used, however, in the estimation of iron, reduction cannot be carried out by means of zinc; for although zinc salts do not interfere with the reaction between dichromate and ferrous salt, they do react with the external indicator (potassium ferricyanide), and make its indications of doubtful value. Magnesium may be used instead, but this metal is expensive. It is usual to employ either stannous chloride or ammonium bisulphite to reduce any ferric iron. (See Potassium Dichromate, p. 30.)

Question 62.—What weight of potassium dichromate will be required to yield 8 grm. of oxygen for oxidizing purposes?

Exercise 69.—**Make half a litre of $\frac{N.}{10}$ potassium dichromate, and test its strength by means of a ferrous salt. State its exact value thus:—**

1 cu. cm. = ? grm. $K_2Cr_2O_7$; ? grm. Fe''; ? grm. O_2.

Directions.—1. Fuse some $K_2Cr_2O_7$ crystals in a porcelain dish to drive off included water, allow to become cold, and weigh out the necessary quantity. (See p. 30.)

2. The ferrous salt used may be either Mohr's salt or good crystals of ferrous sulphate. The latter is preferred by some chemists, provided H_2SO_4 is added to the water to hinder oxidation.

3. Equation:—

$$6\,(Am_2SO_4),\ FeSO_4 + K_2Cr_2O_7 + 7\ H_2SO_4$$
$$= 6\,(Am_2SO_4) + K_2SO_4 + 3\ Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + 7\ H_2O.$$

4. Dichromate in burette; indicator (external), $K_3FeC_6N_6$.

Question 63.—If in the last exercise the solution of dichromate is found to be not exactly $\frac{N.}{10}$, express its relationship to this value by a factor.

Assuming the Fe'' solution is exactly $\frac{N.}{10}$, and that 25 cu. cm. require 25.2 cu. cm. of the $K_2Cr_2O_7$ solution; this latter will be $\frac{250}{252} \times \frac{N.}{10}$, or $\frac{N.}{10} \times 0.992$.

Question 64.—What weight of potassium dichromate is equivalent as an oxidizer to 1 grm. of potassium permanganate?

Exercise 70.—**A sample of spathic iron ore provided consists mainly of ferrous carbonate. By means of $\frac{N.}{10}$ dichromate, find the percentage of ferrous iron present.**

Directions.—1. Dissolve an accurately weighed quantity of about 1 grm. of the ore in dilute acid, and make up to 100 cu. cm. with recently boiled and cooled distilled water ("boiled out" water), and mix well. See Ex. 59 for means of preventing oxidation. This is especially necessary if HCl is used.

2. Let insoluble matter settle, and neglect it as it occupies so little volume.

3. Equation shows 4.9 grm. $K_2Cr_2O_7 = 5.58$ grm. Fe″.

Question 65.—It is found that 25 cu. cm. $\frac{N.}{10}$ ferrous solution require respectively 17.5 cu. cm. of $KMnO_4$ solution and 18.2 cu. cm. of $K_2Cr_2O_7$ solution to convert the ferrous iron to ferric. How many grammes of available oxygen are there in 1 l. of each solution?

Question 66.—On titrating a dichromate solution with $\frac{N.}{8}$ $FeSO_4$, it was found that 25 cu. cm. of the latter required 20 cu. cm. of the former to oxidize the iron. What weight of CrO_3 was present in 1 l.?

Exercise 71.—Find the percentage of iron in a sample of hematite, using $\frac{N.}{10}$ $K_2Cr_2O_7$.

Directions.—1. Finely powder the sample; dry it, and weigh out about 1 grm. by difference, and dissolve in small quantity of concentrated HCl diluted with equal volume of H_2O.

2. Proceed by method A or B.

Method A.—Reduction of iron with ammonium bisulphite (NH_4HSO_3). [Made by bubbling SO_2 through strong NH_4OH, contained in a test-tube standing in water, till any crystals which may form redissolve and the liquid smells strongly of SO_2.]

(i) Neutralize as nearly as possible the acid iron solution with AmOH.

(ii) Add 5 to 10 cu. cm. of the NH_4HSO_3 solution, and boil.

(iii) Mix 10 cu. cm. concentrated H_2SO_4 with 10 cu. cm. H_2O, add it to the solution, and continue boiling till all SO_2 has been expelled. (20 minutes.)

(iv) Cool quickly, and make up to 100 cu. cm. with boiled out and cooled water. This solution should work with $\frac{N.}{10}$ $K_2Cr_2O_7$.

(v) Indicator: freshly-made solution of $K_3FeC_6N_6$.

Method B.—Reduction of iron with good $SnCl_2$.

(i) Cool and make up the iron solution to 100 cu. cm. This will contain a fair excess of HCl, which is necessary in this method.

(ii) Boil up each quantity of ferric solution withdrawn, and add $SnCl_2$ solution, one drop only at a time, till the red colour *just disappears*, i.e. till the ferric iron is reduced. (Look at a piece of white paper through the liquid.) A *very slight* excess of $SnCl_2$ will probably now be present, which must be oxidized to prevent it reducing any $K_2Cr_2O_7$.

(iii) Cool somewhat, and add a few drops of $HgCl_2$ solution (2 cu. cm. should be plenty), when some cloudiness due to HgCl should be seen. This precipitate of mercurous chloride has no action on $K_2Cr_2O_7$.

(iv) Titrate as soon as possible.

(v) Indicator: freshly-made solution of $K_3FeC_6N_6$.

3. Equation:—$6\,FeCl_2 + K_2Cr_2O_7 + 14\,HCl$
$= 6\,FeCl_3 + 2\,KCl + 2\,CrCl_3 + 7\,H_2O$.

Why cannot zinc be used for reduction purposes in the above exercise?

Question 67.—You are asked to find the strength of some potassium permanganate which is about $\frac{N.}{10}$, and are provided with acid potassium oxalate (C_2O_4HK). How much of the latter salt would you require to make 1 l. of $\frac{N.}{10}$ strength? This solution may also be used for standardizing alkali. Would you assume it to be $\frac{N.}{10}$ also for this purpose? If not, state its relationship to $\frac{N.}{10}$ strength.

Question 68.—Two solutions containing respectively potassium permanganate and ferrous iron are roughly decinormal. Being provided with pure solid potassium dichromate, how would you find the exact strength of the permanganate solution?

CHAPTER VIII

Methods involving Indirect Oxidation

IODOMETRY

Many examples of oxidation by halogens will be familiar to you. In each case the oxygen is derived from water through its reaction with the halogen. When an aqueous solution of chlorine is exposed to direct sunlight a small quantity of oxygen is actually set free, and may be collected, though the greater part goes to form chloric acid.

$$8\,Cl_2 + 8\,H_2O = O_2 + 14\,HCl + 2\,HClO_3.$$

Exercise 72.—Examine the power of each halogen to oxidize different substances.

Directions.—The following experiments will serve as examples:—

1. Test some solution of $FeSO_4$ for ferric salt, and repeat after adding a few drops of chlorine water.

2. To 1 cu. cm. of $SnCl_2$ solution add bromine water in slight excess, i.e. till the solution remains permanently red. Test for $SnCl_2$ with $HgCl_2$.

3. Test some H_2SO_3 solution for H_2SO_4. Repeat after adding a little solution of iodine, and contrast the results.

Of these three halogens, that most generally useful for making standard solutions is *iodine*, for the following reasons:—

(i) It is more easily purified than either of the others. (ii) Being solid, it is most easily handled and weighed out. (iii) Excess used in a titration can be most readily detected, partly by its colour, and particularly by the starch test. Although not very soluble in water, it dissolves readily in the presence of potassium iodide, which does not interfere with its reactions.

Exercise 73.—Make 500 cu. cm. of approximately deci-normal solution of iodine.

Directions.—1. *To Purify the Iodine.*—If the purity of your sample is doubtful, powder up rather more than you require, and heat it in a porcelain dish on a water-bath for 15 min. Next, mix it thoroughly with about $\frac{1}{10}$th its weight of pure KI well ground up; cover the mixture with a well-fitting inverted funnel or dish, and heat on a sand-bath till the iodine has sublimed into the inverted vessel. The sublimed iodine may be assumed to be pure.

2. *Weighing out.*—The equivalent of iodine being 126.92—the same as its atomic weight, $\frac{1}{2}$ l. of $\frac{N.}{10}$ solution should contain 6.346 grm. But the volatility of iodine renders it doubtful whether the difference between two weighings represents exactly the weight dissolved; and so it is usual to take rather more than the theoretical quantity. Put about $6\frac{1}{2}$ grm. into a 500-cu.-cm. measuring-flask.

3. *Solution.* — Half-fill the flask with water, and add 10 grm. of pure KI—or more if required to complete the solution of the iodine. Add water to the mark, and mix thoroughly.

4. *Preservation of Solution.*—Keep in a dark place in a stoppered bottle, properly labelled.

Standard Sodium Thiosulphate.—It was seen in Ex. 16 that the colour due to iodine disappeared on the addition of sodium thiosulphate. The reaction between these two substances is expressed by the equation—

$$\underbrace{I_2}_{253.8} + \underbrace{2\,Na_2S_2O_3}_{316.3} = Na_2S_4O_6 + 2\,NaI.$$

253.84 grm. of iodine reacting with 316.28 grm. of the thiosulphate (or with 496.44 grm. of the pentahydrate crystals, $Na_2S_2O_3$, $5\,H_2O$) produce the tetrathionate and sodium iodide; and since free iodine is so readily detected, the end-point of the reaction can be easily determined. By the combined use of these reagents a much larger number of estimations become possible.

The weight of thiosulphate crystals which correspond with 126.92 grm. of iodine is 248.22 grm., hence decinormal thiosulphate will require 24.82 grm. of crystals containing 15.81 grm. of $Na_2S_2O_3$ to the litre. It will be noticed that this weight of crystals contains two equivalent weights of sodium; but just as decinormal solutions of permanganate and dichromate contain that weight per litre which can yield $\frac{1}{10}$th of the gramme-equivalent weight of oxygen, so a litre of decinormal thiosulphate must contain that weight of the salt which can react with $\frac{1}{10}$th of the gramme-equivalent of iodine. (See also p. 97.)

Exercise 74.—Make $\frac{1}{2}$ l. of decinormal thiosulphate, and with it determine the strength of the iodine solution made in last exercise.

Directions.—1. Assume the crystals to be pure. This will be ascertained in a later exercise. Crush up the crystals ($Na_2S_2O_3$, $5\,H_2O$), and dry the powder well between filter paper. Accurately weigh out 12.41 grm., dissolve in water, and make up to 500 cu. cm.

2. Thiosulphate in burette.

3. Indicator: starch solution. (See Ex. 13.)

This is best added towards the end of the reaction; that is, when only sufficient iodine is left to produce a faint yellowish colour. Shake up after each addition of $Na_2S_2O_3$. The reaction is complete when the blue colour is just destroyed.

4. Either dilute your iodine solution to $\frac{N.}{10}$ strength, or find the factor expressing its relationship to this value. For example—

If 25 cu. cm. of I solution = 26.5 cu. cm. $\frac{N.}{10}$ $Na_2S_2O_3$,

the 25 cu. cm. require dilution to 26.5 cu. cm., and so on.

Or, its strength may be given as $\left[\frac{N.}{10} \times 1.06\ \mathrm{I.}\right]$.

Use of Sodium Bicarbonate ($NaHCO_3$).—In the exercise just completed, the conversion of thiosulphate into the more highly oxidized tetrathionate was accomplished by the splitting off of a portion of the positive radical, which then united with iodine. But in many estimations oxygen is actually supplied to the reducing substance from the water present, whose hydrogen then combines with iodine to form hydriodic acid. The reaction, however, is reversible, and may be represented—

$$H_2O + I_2 \rightleftarrows 2\,HI + O.$$

To prevent the backward reaction, the hydriodic acid is neutralized by a suitable alkali—an acid carbonate being found most convenient. Caustic alkali cannot be used, because it reacts with iodine as well as with the acid.

$$2\,NaOH + I_2 = NaIO + NaI + H_2O.$$
$$3\,NaIO = NaIO_3 + 2\,NaI.$$

Normal alkali carbonates are also unsuitable, as they suffer some hydrolysis to caustic soda and acid carbonate, when the former can react with iodine as shown above.

$$Na_2CO_3 + H_2O = NaOH + NaHCO_3.$$

Even the bicarbonates hydrolyse to some slight extent, but unless present in great excess their use introduces practically no error.

Exercise 75.—Prepare some $\frac{N.}{10}$ solution of arsenious oxide and titrate it against your $\frac{N.}{10}$ iodine.

Directions.—1. Unless sure of its purity, resublime sufficient As_4O_6 from a crucible or dish, up into an inverted vessel (a funnel does well) placed over it. This should be done in a fume closet.

2. Arsenious compounds oxidize to the arsenic state in presence of iodine and water, as expressed in the equation—

$$\underbrace{As_4O_6}_{395.8} + \underbrace{4\,I_2}_{1015.4} + 4\,H_2O = 2\,As_2O_5 + \underbrace{8\,HI}_{1023.4},$$

from which it will be evident that $\frac{1}{80}$ mol of As_4O_6 should produce a litre of $\frac{N.}{10}$ solution. 250 cu. cm. will be sufficient for this and later exercises. Time will be saved if you accurately weigh out (by difference) approximately this quantity (about 1.5 grm.) into the graduated flask.

3. *Solution of* As_4O_6.—Probably your best method will be to dissolve it in the least quantity of NaOH with gentle heat, then to prevent reaction of the alkali with iodine neutralize with dilute HCl. Cool, and add water to the mark. Preserve the solution in a bottle properly labelled.

4. To each 25 cu. cm. withdrawn for titration, add 0.75 to 1.0 grm. of powdered $NaHCO_3$ or 10 to 12 cu. cm. of

cold saturated solution, which contains about one-twelfth its weight of the acid carbonate.

5. Iodine solution in burette (glass stopcock).

6. Indicator: 1 cu. cm. starch solution for each quantity titrated. The end-point will be reached when the blue colour persists for five minutes after thorough mixing.

Assuming your As_4O_6 solution to be accurately decinormal, how does the strength of your iodine solution compare with the previous determination?

Note on the quantity of $NaHCO_3$ used. The equation—

$$8\ [\underbrace{HI}_{1023.4} + \underbrace{NaHCO_3}_{672} = NaI + CO_2 + H_2O]$$

combined with that in (2) above indicates that for 396 grm. of As_4O_6, 672 grm. of $NaHCO_3$ are necessary to neutralize the HI formed. 25 cu. cm. of solution prepared in above exercise contain approximately 0.15 grm. As_4O_6, and will require theoretically about 0.25 grm. $NaHCO_3$ to neutralize the HI formed; so that the addition of (0.75 to 1) grm. to each quantity will allow a fair margin of excess, yet not so great as to introduce error.

Question 69.—How would you proceed to estimate an *arsenate* by means of iodine?

Exercise 76.—Find the percentage of antimony in tartar emetic, using $\frac{N.}{10}$ iodine.

Directions.—1. Tartar emetic results from the solution of antimonious oxide (Sb_4O_6) in hydrogen potassium tartrate. In this compound the antimony retains its triad valency, but in the presence of iodine and water it passes into the antimonic state (with a valency of five) as metantimonic acid [$HSbO_3$ or H_2O, Sb_2O_5]. Anhydrous tartar emetic is represented by the formula $K(SbO)C_4H_4O_6$. The equations (i) $Sb_2O_3 + 2\ I_2 + 2\ H_2O = Sb_2O_5 + 4\ HI$; (ii) $K(SbO)C_4H_4O_6 + I_2 + 2\ H_2O = HSbO_3 + KHC_4H_4O_6 + 2\ HI$ show that 253.8 grm. of I = 120.2 grm. of Sb'''.

2. About 1.5 grm. of tartar emetic dissolved up to 100 cu. cm. should work with $\frac{N.}{10}$ iodine.

3. *Caution in using* $NaHCO_3$ *with Tartar Emetic.*—This reagent precipitates the Sb as hydroxide on standing. In order to avoid this, 15 to 20 cu. cm. of a cold saturated solution must be added to each quantity of the antimonious solution just before the iodine is run in.

4. $\frac{N.}{10}$ iodine in burette (glass stopcock).

5. The reaction will be complete when the blue tint persists after mixing.

Exercise 77.—By means of $\frac{N.}{10}$ iodine, find the percentage weight of sulphur dioxide in some freshly-made solution. Also, calculate the volume of gas dissolved in 1 Kg. of the solution.

Directions.—1. With dilute solution of SO_2 the reaction between it and iodine is thus shown:—

$$SO_2 + I_2 + 2\,H_2O = H_2SO_4 + 2\,HI.$$

Consequently 253.8 grm. I = 64.1 grm. SO_2. Ordinary solutions of SO_2 must be well diluted.

2. Find the exact weight of a small quantity of the solution by pouring 3 to 4 cu. cm. into a weighed, stoppered 100-cu.-cm. measuring-flask and weighing again. Escape of gas is thus prevented during weighing.

3. Make up to the mark with recently boiled and cooled distilled water.

4. Iodine in burette. Indicator: starch.

5. Add excess of solid $NaHCO_3$ to each portion taken for titration. 0.5 grm. will be sufficient for each 25 cu. cm. of $\frac{N.}{10}$ iodine used. The total quantity necessary should be ascertained by a rough trial. [There is 0.32 grm. iodine in 25 cu. cm. $\frac{N.}{10}$ solution, which requires rather less than 0.25 grm. $NaHCO_3$ to neutralize the HI produced.]

6. Percentage weight of SO_2 in the solution

$$= \frac{\text{Weight of } SO_2 \text{ found}}{\text{Weight of solution}} \times 100.$$

7. A mol of SO_2 at S.T.P. occupies 22.4 l.

∴ Volume of SO_2 (at S.T.P.) dissolved in 1 Kg. of solution is

$$\frac{\text{grammes of } SO_2 \text{ in 1 Kg. of solution}}{\text{mol of } SO_2} \times 22.4 \text{ l.}$$

Alternative method.—See Ex. 80.

Use of Standard Thiosulphate with Iodine.—So far, the estimation of such reducing agents as SO_2, &c., has been carried out by noting directly the quantity of standard iodine required to oxidize them. But more accurate results can often be obtained by adding excess of iodine and determining the excess with standard thiosulphate. The iodine used in the main reaction can now be found by difference, and the weight of the substance to be estimated can be calculated. Further, various substances such as chlorine, bromine, &c., can displace equivalent weights of iodine from potassium iodide, when the estimation of the expelled iodine furnishes a means of estimating the chlorine, &c. (See also p. 92.)

Exercise 78.—Find the percentage of Na_2SO_3 in some of the commercial compound.

Directions.—1. Weigh out about 1 grm. into a 200-cu.-cm. measuring-flask, and dissolve in a little "boiled-out" water.

2. Add 100 cu. cm. $\frac{N.}{10}$ iodine, which should be in good excess, then about a gramme of $NaHCO_3$; shake up well, add water to the mark, mix, and allow to stand before titrating.

3. Determine excess of I used with $\frac{N.}{10}$ or $\frac{N.}{20}$ $Na_2S_2O_3$. Indicator: starch. End-point when blue colour just disappears after shaking.

4. Equation

$$\underbrace{Na_2SO_3}_{126.1} + \underbrace{I_2}_{253.8} + H_2O = Na_2SO_4 + 2\,HI$$

shows that the weight of pure Na_2SO_3 present is $\frac{126}{254}$th of the iodine used up.

Pure crystals are represented by formula $Na_2SO_3 \cdot 7\,H_2O$.

Exercise 79.—Assuming your $\frac{N.}{10}$ dichromate to be accurately standardized, titrate it against sodium thiosulphate to estimate the purity of the latter.

Directions.—1. Equations

$$\underbrace{K_2Cr_2O_7}_{294.2} + 6\,KI + 14\,HCl = \underbrace{3\,I_2}_{6 \times 126.9} + 8\,KCl + 2\,CrCl_3 + 7\,H_2O$$

$$\underbrace{I_2}_{2 \times 126.9} + \underbrace{2\,Na_2S_2O_3}_{2 \times 158.1} = Na_2S_2O_6 + 2\,NaI$$

show that 2×158.1 grm. $Na_2S_2O_3 = 2 \times 126.9$ grm. I $= \frac{294.2}{3}$ grm. $K_2Cr_2O_7$.

2. Solution of $Na_2S_2O_3$ of suitable strength in burette.

3. Dilute each quantity of $\frac{N.}{10}$ $K_2Cr_2O_7$ taken, add about 1 grm. powdered KI, then 2 to 3 cu. cm. concentrated HCl, and shake up well. Allow to stand a few minutes before running in the $Na_2S_2O_3$. The excess of KI prevents precipitation of I.

Question 70.—What relationship do you find between the volumes of $\frac{N.}{10}$ $K_2Cr_2O_7$ and $\frac{N.}{10}$ $Na_2S_2O_3$ necessary to complete the reaction in Ex. 79? Explain why this should be so.

Exercise 80.—Repetition of Ex. 77. Alternative method, using back titration.

Directions.—1. Weigh out some standard I solution more than sufficient to react with the SO_2 to be taken.

2. Pipette off 10 or more cu. cm. of SO_2 solution, and run it into the I solution with the nozzle below the surface of liquid. Weigh again.

3. Find excess of I by standard $Na_2S_2O_3$.

Exercise 81.—Find the weight of chlorine in 100 grm. of fresh chlorine water.

Directions.—1. Pour about 10 cu. cm. of the chlorine water into a weighed stoppered flask, and find the exact weight taken.

2. Add about 0.5 grm. of solid KI, which is more than sufficient to react with the free chlorine, and shake up well before making up to known volume.

$$\underbrace{Cl_2}_{70.9} + \underbrace{2\,KI}_{331.8} = 2\,KCl + \underbrace{I_2}_{253.8}.$$

3. Find weight of I liberated with standard $Na_2S_2O_3$. Indicator: starch.

4. Weight of Cl in that of solution taken will be $\frac{71}{254}$th of weight of iodine found.

Notes.—(i) Neither chlorine nor bromine reacts with $Na_2S_2O_3$ as iodine does; so

(ii) bromine water may be similarly estimated.

(iii) Excess of KI is often required to keep liberated iodine dissolved.

Question 71.—10 cu. cm. of some bench potash solution had the calculated quantity of chlorine passed into it to convert it into mixed chloride and hypochlorite. After adding excess of potassium iodide and hydrochloric acid, iodine was liberated, and the solution was further diluted to 250 cu. cm. On titrating with thiosulphate, it was found that 25 cu. cm. required 52 cu. cm. $\frac{N.}{10}$ $Na_2S_2O_3$. What was the approximate strength of the bench potash?

Since 25 cu. cm. diluted iodine solution required 52 cu. cm.

$\frac{N.}{10}$ $Na_2S_2O_3$, the former was very nearly $\frac{N.}{5}$; and, consequently, before dilution, 4 N.

$$\begin{aligned}
\text{Also } 4\,(126.92)\text{ grm. I} &= 4\,(35.46)\text{ grm. Cl,}\\
\text{and equations (i) } KOCl + 2\,HCl &= KCl + Cl_2 + H_2O,\\
\text{(ii) } Cl_2 + 2\,KOH &= KCl + KOCl + H_2O\\
\text{show that } 4\,(35.46)\text{ grm. Cl} &= 2\,(90.6)\text{ grm. KOCl,}\\
\text{and } 2\,(90.6)\text{ grm. KOCl} &= 4\,(56)\text{ grm. KOH.}
\end{aligned}$$

∴ The bench solution was approximately 4 N.

Exercise 82. — Find the percentage weight of chlorine available for bleaching purposes in a sample of bleaching powder.

Directions.—1. The "available" chlorine is set free from bleaching powder during ordinary bleaching processes by dilute acid, and does not include that present as chlorate or chloride. It is supposed to be combined as calcium chloro-hypo-chlorite, Ca(OCl)Cl. (Odling.) Acetic acid is usually employed in the estimation, as it does not decompose other compounds present.

$$\underbrace{Ca(OCl)Cl}_{127} + 2\,CH_3.COOH = (CH_3.COO)_2Ca + \underbrace{Cl_2}_{70.9} + H_2O.$$

2. *Preparation of solution.*—Weigh out accurately about 1 grm. of the powder into a clean mortar. Add a few cubic centimetres of water, and grind up as finely as possible. Decant the aqueous portion without loss into a 250-cu.-cm. measuring-flask, then add a second quantity of water to the residue and grind up again, and pour off the milky liquid as before. Repeat this process as long as any powder subsides. Add rinsings to the flask, also water to fill up to mark; mix, and *titrate at once.* (N.B.)

3. *Titration*, &c.—Shake up the liquid well before withdrawing each quantity. Take 50 cu. cm. each time, and add approximately 0.5 grm. solid KI together with about

5 cu. cm. dilute acetic acid. Use $\frac{N.}{10}$ $Na_2S_2O_3$, and add the starch indicator towards the end of the reaction.

4. Combining equations previously given, we see that 316.3 grm. $Na_2S_2O_3$ = 253.8 grm. iodine = 70.9 grm. chlorine. ∴ Total weight of "available" chlorine in the bleaching powder taken = $\frac{31}{316}$ × weight of $Na_2S_2O_3$ necessary to react with the whole of the iodine displaced.

Question 72.—Assuming that all the chlorine found existed as chloro-hypochlorite, what proportion of the bleaching powder consisted of this salt?

Exercise 83.—Find the weight of available oxygen in 1 l. of $KMnO_4$ solution by means of potassium iodide and sodium thiosulphate.

Directions.—1. See those for Ex. 78. Reactions are—

$$\underbrace{2\,KMnO_4}_{316} + 10\,KI + 8\,H_2SO_4 = 6\,K_2SO_4 + 2\,MnSO_4 + \underbrace{5\,I_2}_{10\times 126.9} + 8\,H_2O$$

$$\underbrace{I_2}_{2\times 126.9} + \underbrace{2\,Na_2S_2O_3}_{2\times 158.1} = Na_2S_4O_6 + 2\,NaI,$$

which show that 10 × 158.1 grm. $Na_2S_2O_3$ = 316 grm. $KMnO_4$, or 0.01581 grm. $Na_2S_2O_3$ = 0.00316 grm. $KMnO_4$. These weights respectively being contained in 1 cu. cm. of $\frac{N.}{10}$ solution, it follows that should the $KMnO_4$ solution be $\frac{N.}{10}$, an equal volume of $\frac{N.}{10}$ $Na_2S_2O_3$ solution will be required.

2. 1 grm. KI and about 20 cu. cm. dilute H_2SO_4 should be sufficient for each 25 cu. cm. of $KMnO_4$, assuming it to be near $\frac{N.}{10}$.

3. Weight of available oxygen is $\frac{80}{316}$ of the weight of $KMnO_4$ found. (See p. 73.)

Exercise 84.—Find the percentage of copper in some copper sulphate crystals by means of potassium iodide and sodium thiosulphate.

Directions.—1. The following method may be used where we have *neutral* solutions of copper salts. Equation:—

$$\underbrace{2\,CuSO_4,\ 5\,H_2O}_{2\times 249.7} + \underbrace{4\,KI}_{4\times 166} = Cu_2I_2 + 2\,K_2SO_4 + \underbrace{I_2}_{2\times 126.9}.$$

$$\therefore\ 126.9 \text{ grm. I} = 249.7 \text{ grm. crystals.}$$

2. *Find weight of crystals necessary* to make 250 cu. cm. solution suitable to work with $\frac{N.}{10}$ $Na_2S_2O_3$. 250 cu. cm. $\frac{N.}{10}$ iodine contain approximately 3 grm. of iodine, which will be liberated from KI by $\frac{249.7}{126.7} \times 3$, or approximately 6 grm. of $CuSO_4$, $5\,H_2O$.

3. *Find weight of* KI *necessary.*—25 cu. cm. of the copper solution contain approximately 0.6 grm. of the crystals, which will require $0.6 \times \frac{4 \times 166}{2 \times 249.7}$, or about 0.8 grm. KI.

4. Weigh out accurately about 6 grm. of powdered selected crystals, and dissolve up to 250 cu. cm.

5. To each 25 cu. cm. withdrawn for titration add 1 to 1.5 grm. powdered KI. This will be in sufficient excess. Neglect the dirty-white precipitate of Cu_2I_2, and titrate at once with $\frac{N.}{10}$ $Na_2S_2O_3$.

6. Weight of copper in crystals taken

$$= \frac{63.6}{126.9} \times \text{weight of I liberated.}$$

Exercise 85.—Find the percentage weight of hydrogen peroxide contained in the sample previously estimated, by means of its reaction with potassium iodide. (Kingzett's method.)

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of PHARMACY

Directions.—1. Equations

$$\underbrace{H_2O_2}_{34} + \underbrace{2\,KI}_{2\times 166} + H_2SO_4 = K_2SO_4 + \underbrace{I_2}_{2\times 126.9} + 2\,H_2O$$

$$\underbrace{I_2}_{2\times 126.9} + \underbrace{2\,Na_2S_2O_3}_{2\times 158.1} = Na_2S_4O_6 + 2\,NaI$$

show that 316 grm. $Na_2S_2O_3$ = 34 grm. H_2O_2.

2. *Quantity of* KI *necessary*. Equation shows 332 grm. KI are required to react with 34 grm. H_2O_2, the proportion being roughly 10 : 1. Ordinary laboratory solution of H_2O_2 yields, at most, twenty times its volume of oxygen; so 1 l. may give off approximately 30 grm. of the gas, or contain about 60 grm. H_2O_2. 1 cu. cm. of the solution (containing 0.06 grm. H_2O_2) requires therefore 0.6 grm. KI; so for every cubic centimetre of the H_2O_2 solution used add 1 to 1.5 grm. KI.

3. *Quantity of* H_2SO_4 *to be added.*—It is found that this must be in considerable excess of the theoretical quantity to give good results, although the reason is not clear.

4. *Process.*—Into a weighed 100-cu.-cm. measuring-flask pour about 10 cu. cm. H_2O_2 solution, and find its exact weight.

Add 50 cu. cm. dilute H_2SO_4 and 10 to 15 grm. powdered KI. Dissolve, and add water to the mark. Allow to stand 5 min., and warm each portion taken for titration with $\frac{N.}{10}$ $Na_2S_2O_3$.

Note.—The above should give more accurate results than the permanganate method (Ex. 68). How do your results agree?

Question 73. — Roughly speaking, what volume of oxygen reckoned at S.T.P. could you obtain from 1 l. of the above solution?

Exercise 86.—Using $\frac{N.}{10}$ arsenious oxide solution, find the percentage of available chlorine in the sample of bleaching powder previously examined, and compare your results.

Directions.—1. The reaction may be represented thus:

$$\underbrace{As_4O_6}_{395.8} + 4\,CaOCl_2 = 2\,As_2O_5 + 4\,CaCl_2.$$

395.8 grm. As_4O_6 take 64 grm. of oxygen from the bleaching powder. The chlorine equivalent (obtained by other means) = 283.7 grm. So the "available" chlorine in the bleaching powder examined will be $\frac{284}{396}$ times the weight of As_4O_6 used.

If the As_4O_6 is made exactly $\frac{N.}{10}$, each cubic centimetre used = 0.003546 grm. chlorine.

2. Prepare a fresh solution of the bleaching powder, as directed in Ex. 80, and titrate at once, shaking up well before withdrawing each portion.

3. $\frac{N.}{10}$ As_4O_6 was made in Ex. 74. Put this in burette.

4. Make two titrations, using moistened iodized starch paper as external indicator. (See Ex. 17.) When no blue colour is produced by a drop withdrawn on a clean glass rod and placed upon the paper, all hypochlorite is decomposed and the reaction is complete.

5. Make two backward titrations as follows: Run into the bleaching-powder solution a known volume of the $\frac{N.}{10}$ As_4O_6 in good excess; add 1 cu. cm. starch solution, and determine the excess of As_4O_6 by $\frac{N.}{10}$ iodine. The end-point is shown by permanent blue tint after shaking. The results should agree with those of 4.

Highly oxidized substances, such as manganese dioxide, lead dioxide, potassium chromate, &c., which liberate chlorine from hydrochloric acid, may be estimated by distilling off the liberated chlorine into solution of iodide, when the iodine equivalent of the chlorine is set free, and may be determined in the usual way.

Exercise 87.—Find the weight of chlorine set free from hydrochloric acid during its reaction with 1 grm. formula weight of manganese dioxide.

Directions.—1. Use Bunsen's distillation method. The apparatus is shown in fig. 14. A small flask (50 cu. cm.) is fitted with a bulbed tube or common pipette bent at an acute angle above the bulb, and passing through a cork well soaked in melted paraffin. The stem of the pipette is thrust far enough into a small retort (100 cc. will do) fixed in an inverted position, so that the end appears under the bulb. The retort should contain 2 to 2.5 grm. of KI dissolved in about 50 cu. cm. of water, and be placed in a dish of cold water to keep its contents cool.

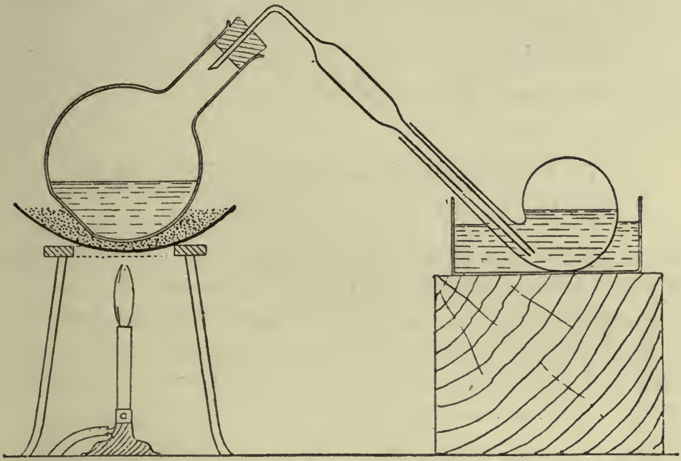

Fig. 14

2. Grind up a little pure dry MnO_2 to a fine powder, and weigh out by difference about 0.3 grm. into the flask. Also place in the flask a piece of magnesite ($MgCO_3$) about as big as a large pea. This latter by slow reaction with the acid will produce a steady stream of CO_2, and lessen the chances of regurgitation of KI solution into the flask.

Add 15 to 20 cu. cm. concentrated HCl, at once insert cork with delivery tube, and apply *gentle* heat.

3. The reaction should be complete when about one-third of the acid liquid has passed over. Towards the end withdraw the pipette so that its nozzle only just dips into the iodine solution, and boil up to expel the last traces of chlorine.

4. Pour the iodine solution into a suitable measuring-flask (100 cu. cm. or 200 cu. cm.), and add rinsings both of retort and pipette. Add water to mark, and mix well.

5. Titrate with $\frac{N.}{10}$ $Na_2S_2O_3$.

6. Equations—

$$\begin{aligned} &\text{(i)}\ MnO_2 + 4\,HCl &&= MnCl_2 + Cl_2 + 2\,H_2O, \\ &\text{(ii)}\ Cl_2 + 2\,KI &&= I_2 + 2\,KCl \end{aligned}$$

show that 253.8 grm. I = 70.9 grm. Cl = 86.9 grm. MnO_2. How does this agree with your result?

Question 74.—It was found that when 0.5 grm. of pyrolusite was treated by the above method, 1.1682 grm. of iodine were liberated. What proportion of manganese dioxide did the sample contain?

Exercise 88.—Find the proportion of chromium trioxide in potassium dichromate.

Directions.—1. Follow generally those given in last exercise.

2. The equation—

$$\underbrace{K_2Cr_2O_7}_{294.2} + 14\,HCl = 2\,CrCl_3 + 2\,KCl + \underbrace{3\,Cl_2}_{212.8} + 7\,H_2O$$

shows the weight relationship between the chromate and chlorine expelled. One-third of a formula weight of $K_2Cr_2O_7$ (viz. 98 grm.) liberates as much chlorine as formula weight (87 grm.) of MnO_2, so that about the same quantities may be taken as before.

Potassium dichromate may be regarded as $K_2O(CrO_3)_2$.

CHAPTER IX

Methods involving Precipitation

In the exercises following, precipitates are formed which are regarded as insoluble in the solutions finally obtained. But although the end-point of each reaction theoretically coincides with completion of precipitation, it is usually necessary to rely upon the evidence of some indicator to mark the point with precision.

USE OF SILVER NITRATE

A method of estimating silver and halides in their soluble salts has been suggested in Exercise 10. A standard solution of one of the reacting substances can be used to estimate the other—either by noting when precipitation ceases, or by some other evidence, such as that afforded, in neutral solutions, by the permanence of a trace of red silver chromate. A gramme formula weight of silver nitrate contains 108 grm. of silver, the whole of which is necessary to displace 1 grm. of hydrogen from acid. A "molar" solution of the nitrate is therefore of normal strength, and must contain 169.9 grm. of $AgNO_3$ per litre.

1 cu. cm. decinormal silver nitrate
= 0.01699 grm. $AgNO_3$, or 0.01079 grm. Ag., or 0.003546 grm. Cl.; and so on.

Since we cannot rely on the purity of ordinary crystals of this salt, nor can we purify them quickly, it is customary to make a solution somewhat above the strength required, and determine its exact value by titration against sodium chloride—pure crystals of which can be easily obtained—then dilute the silver solution to the required strength. 58.46 grm. of sodium chloride contain the gramme-equivalent of chlorine; consequently a decinormal solution should contain 5.846 grm. of the salt in 1 l.

Exercise 89.—Prepare 10 to 20 grm. of pure crystals of sodium chloride, and with them make $\frac{1}{2}$ l. of decinormal solution.

Directions.—1. Dissolve as much common salt as possible in about 75 cu. cm. of cold water, and filter if not clear.

2. Pass HCl gas first through a few cu. cm. of water to wash it, then into the solution until sufficient small crystals have been precipitated. The delivery-tube should terminate in a funnel whose rim should just touch the water. Blocking up the delivery-tube by solid NaCl will thus be avoided. (See fig. 15.)

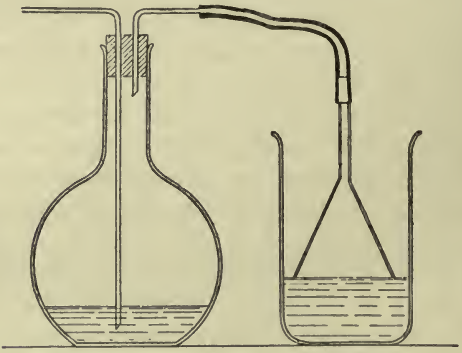

Fig. 15

3. Pour off the liquor, transfer the crystals to a filter, and wash first with concentrated HCl, and finally with a little alcohol.

4. Dry thoroughly in an air oven, and allow to cool in a desiccator before weighing out.

5. ½ l. of $\frac{N.}{10}$ solution should contain 2.923 grm. NaCl, which may be weighed out on a watch-glass.

Exercise 90.—Make ½ l. $\frac{N.}{10}$ silver nitrate.

Directions. — 1. Weigh out by difference rather more than the theoretical quantity of powdered crystals, 8.5 to 9 grm., into a ½-l. graduated flask; dissolve, and add distilled water to the mark, and mix well.

2. *Titrate the solution* against $\frac{N.}{10}$ NaCl. Since no free acid is present, *Mohr's method* of determining the end-point may be used. One or two drops of K_2CrO_4 are added to each portion of liquid withdrawn for titration. Which solution should be in the burette? A white precipitate of silver chloride should be formed together with transient red silver chromate (Ag_2CrO_4). When, after shaking up, a trace of the latter persists and slightly colours the precipitate, the reaction between silver salt and halide is complete.

It may be recalled that AgCl is somewhat soluble in presence of NaCl; but none of the latter salt remains when the reaction is complete.

3. Equation—

$$\underbrace{AgNO_3}_{169.9} + \underbrace{NaCl}_{58.5} = AgCl + NaNO_3$$

shows that 58.5 grm. NaCl = 169.9 grm. $AgNO_3$.

N.B.—Preserve the solution in a brown-tinted glass bottle with a glass stopper. Wooden or rubber corks decompose $AgNO_3$. If a colourless glass bottle must be used, paste black paper round it, and keep it in the dark. Label it 1 cu. cm. = (?) grm. $AgNO_3$.

Exercise 91.—A solution provided has been made by dissolving about 5 grm. of silver in excess of nitric acid, and making up to 1 l. Find the total weight of nitric acid used.

Directions.—1. Ascertain the *weight of free* HNO_3 by means of suitable standard alkali.

2. *Weight of combined acid* can be calculated from that of silver found. 107.9 grm. of Ag = 63 grm. HNO_3. To estimate the Ag in the acid solution use either (A) standard NaCl, or (B) standard thiocyanate.

A. *Standard* NaCl *used.*—The end-point may be determined by

(i) *Mohr's method*, if the free acid in each quantity titrated is first carefully neutralized.

(ii) *Gay-Lussac's method*, in which no indicator is used, but the reaction is considered complete when one drop of the added solution produces no further precipitate or cloudiness. This is often difficult to determine, and the method is apt to become tedious; but if the acid solution is warmed and agitated, the precipitate coagulates more easily. Rakow recommends the addition of a few drops of CS_2 towards the end of each titration as an aid to coagulation.

B. For use of *standard thiocyanate*, see Ex. 94.

Exercise 92.—A solution contains chlorides of calcium and potassium only. Find the weight of calcium salt which has been mixed with 1 grm. of the potassium compound.

Directions.—1. Since no free acid is present, find the total chlorine in a definite volume with standard $AgNO_3$ as in Ex. 90.

2. Find the weight of calcium salt in an equal volume either by means of (A) standard oxalic acid or (B) standard sodium carbonate.

A. *By Standard Oxalic Acid* $(COOH)_2$.

(i) Transfer 50 cu. cm. of solution to a 250-cu.-cm.

graduated flask, and add a known volume of N. oxalic acid, taking care that more is added than sufficient to precipitate all the calcium present.

(ii) Add sufficient AmOH to neutralize the excess of oxalic acid and make the solution alkaline.

(iii) Boil for five minutes, noting that NH_3 is escaping from the boiling solution all the time.

(iv) Cool, add water to the mark, and mix well. The volume occupied by the precipitate is neglected.

(v) Filter off the precipitate (hydrated calcium oxalate) through a paper not previously wetted.

(vi) Determine the unprecipitated oxalic acid by means of $\frac{N.}{10}$ $KMnO_4$.

(vii) Weight of $(COOH)_2$ used to precipitate the calcium in 50 cu. cm. of given solution can now be found by difference, and the weight of $CaCl_2$ calculated. 90 grm. $(COOH)_2$ = 111 grm. $CaCl_2$.

(viii) From the total chlorine found in 1 subtract that combined with calcium. It should be $\frac{70.9}{111} \times$ weight of $CaCl_2$ found. That combined with potassium is now found by difference, from which the weight of KCl can be calculated.

B. *By Standard Sodium Carbonate*, Na_2CO_3. Precipitate the calcium as carbonate, using N. Na_2CO_3. Do not add AmOH, but boil to make precipitation complete. Filter off precipitate as in (v) above. Find the excess of Na_2CO_3 with $\frac{N.}{10}$ acid. The weight of $CaCl_2$ in the quantity of solution taken is $\frac{111}{106} \times$ weight of Na_2CO_3 used in the precipitation.

Question 75.—If barium chloride is substituted for the calcium salt in the foregoing exercise, what precaution must be taken in using potassium dichromate for indicator?

MIXTURES OF TWO SALTS CONTAINING ONE RADICAL IN COMMON

Question 76.—1 grm. of a mixture of sodium and potassium chlorides was found to require 2.812 grm. of silver nitrate to precipitate the whole of the chlorine present. Calculate the percentage of each chloride in the mixture.

If the powder consisted wholly of KCl, the equation—

$$\underbrace{KCl}_{74.56} + \underbrace{AgNO_3}_{169.89} = AgCl + KNO_3$$

shows that 1 grm. would require $\frac{169.89}{74.56}$ or 2.2786 (nearly) grm. of $AgNO_3$.

Similarly, if it consisted wholly of NaCl, 1 grm. would require $\frac{169.89}{58.5}$ or 2.9061 (nearly) grm. of $AgNO_3$. It is evident, therefore, that the mixture requiring 2.812 grm. must consist mainly of NaCl; and—

$$\frac{\text{Weight of NaCl}}{\text{Weight of KCl}} = \frac{2.812 - 2.2786}{2.9061 - 2.812} = \frac{0.5344}{0.0941}.$$

$$\text{Per cent weight of NaCl} = \frac{0.5344}{0.6275} \times 100 = 85 \text{ per cent.}$$

$$\text{,, \quad ,, \quad ,, KCl} = \frac{0.0941}{0.6275} \times 100 = 15 \quad \text{,,}$$

Note.—In practice, however, good results can be obtained only when the proportions are not widely different.

Question 77.—In another experiment a mixture of the same two salts was found to contain 55 per cent of chlorine. Find the proportion of each chloride present.

Had it all been—

NaCl there would have been 60.66 per cent Cl.
KCl ,, ,, ,, 47.56 ,, ,,

Since 55 per cent Cl has been found—

$$\frac{\text{Weight of NaCl}}{\text{Weight of KCl}} = \frac{55 - 47.56}{60.66 - 55} = \frac{7.44}{5.66}.$$

The mixture, therefore, consists of 56.8 per cent NaCl and 43.2 per cent KCl.

Question 78.—1 grm. of a mixture of sodium chloride and sodium bromide was found to require 2 grm. of silver nitrate for complete precipitation. Find the percentage composition of the mixture.

LIEBIG'S METHOD OF ESTIMATING SIMPLE CYANIDES

Silver nitrate behaves somewhat differently with these compounds. When added to potassium cyanide solution silver cyanide does not appear as a permanent precipitate as long as any excess of potassium cyanide remains in the solution, but forms with it a complex soluble salt, potassium argenticyanide, $KAgC_2N_2$. When no free potassium cyanide remains, further addition of silver nitrate causes the break up of the double cyanide, and a precipitate ($AgCN$) at once forms.

$$AgNO_3 + KAgC_2N_2 = 2\,AgCN + KNO_3.$$

Standard silver nitrate can therefore be used to estimate potassium cyanide if we bear in mind this peculiarity. The appearance of precipitate marks the point when the salts have been mixed in the proportion of one equivalent of silver nitrate to two of potassium cyanide, as expressed in the equation—

$$\underbrace{AgNO_3}_{169.9} + \underbrace{2\,KCN}_{130.2} = KAgC_2N_2 + KNO_3.$$

It will be noted that whereas in titrating halides the end-point is reached when the precipitate *ceases to form*, with cyanides this condition occurs when a trace of permanent precipitate *first appears*. Another point to be remembered is that metallic halides give no precipitate with silver nitrate as long as any free potassium cyanide exists in the solution; consequently the appearance of precipitate, even should a halide be present, marks the end-point of the same reaction.

Exercise 93.—Find the percentage of KCN in some of the solid salt by Liebig's method.

Directions.—1. The equation given above shows that a solution of 2 to 3 grm. of the solid in 100 cu. cm. should work with $\frac{N.}{10}$ $AgNO_3$. Dissolve up this quantity to 100 cu. cm. and mix well.

2. Use $\frac{N.}{10}$ $AgNO_3$ in burette.

3. *Caution.*—Do not risk sucking up the poisonous solution into a pipette. Run out the required quantities from a burette.

4. Stand the beaker upon a dark surface during titration, to be able to detect the first traces of permanent precipitate.

Question 79.—The presence of ammonia in the solution prevents the precipitation of silver cyanide or chloride. Can you suggest a way of meeting this difficulty?

USE OF POTASSIUM (OR AMMONIUM) THIOCYANATE

Exercise 94.—Examine the behaviour of potassium thiocyanate with silver nitrate in neutral and in acid (nitric) solution; also when ferric and other salts are present in addition.

Directions.—1. Try simple solutions of (*a*) $AgNO_3$, (*b*) $FeCl_3$, (*c*) $Am_2Fe_2(SO_4)_4$ among others, both neutral and acidified.

2. Add KCNS solution drop by drop (i) to a mixture of solutions of $AgNO_3$ and iron alum until some striking change appears; (ii) to another quantity of similar solution

after acidifying with a little HNO_3. What effect has the acid upon the colour due to the iron?

3. Repeat 2 after adding some other salt in addition, such as lead acetate, copper sulphate, &c.

The results should show, first, that silver thiocyanate is insoluble in water and dilute nitric acid; secondly, that in the reaction between silver salt and thiocyanate in the presence of ferric salt, directly the silver is precipitated a brown compound is formed—ferric potassium thiocyanate [$Fe(CNS)_3$, 9 KCNS, 4 H_2O], although some other metallic salts are present. The ferric salt acts as an excellent indicator, as the brown colour can usually be detected instantly.

For the estimation of silver, standard thiocyanate offers several advantages over standard sodium chloride. This is *Volhard's* method.

Exercise 95.—Prepare 500 cu. cm. of $\frac{N.}{10}$ potassium thiocyanate.

Directions.—1. The reaction with $AgNO_3$ is given by the equation—

$$\underbrace{AgNO_3}_{169.9} + \underbrace{KCNS}_{97.2} = AgCNS + KNO_3,$$

which shows the equivalent quantities of the reacting salts. Since the thiocyanate is deliquescent, we can only make a first solution approximate to the required strength. About 5 grm. dissolved up to 500 cu. cm. should produce a solution slightly above $\frac{N.}{10}$.

2. Find the exact strength by titration with $\frac{N.}{10}$ $AgNO_3$. Use the burette for KCNS. The indicator is a cold saturated solution of iron alum, 3 cu. cm. of which should be added to each 25 cu. cm. of silver solution, together with enough HNO_3 (usually about 5 cu. cm. is sufficient) to destroy the colour. (See notes below, p. 116.)

3. The end-point is reached when the liquid remains slightly brown after shaking up. It should be viewed on a white surface.

4. Calculate the strength of the KCNS solution on the assumption that $AgNO_3$ is accurately $\frac{N.}{10}$. The weight of KCNS in the average volume used $= \frac{97}{170}$ of the weight of $AgNO_3$ in 25 cu. cm.

5. Label the bottle containing the KCNS with the strength found, or else reduce it to $\frac{N.}{10}$. Should it be found that 25 cu. cm. $\frac{N.}{10}$ $AgNO_3$ = 24.5 cu. cm. KCNS, evidently 24.5 cu. cm. KCNS should be diluted to 25 cu. cm. when 1 cu. cm. = 0.00972 grm. KCNS.

Notes.—(i) Specially prepare the *nitric acid* by diluting concentrated acid with an equal volume of water and boiling till quite colourless.

(ii) If *iron alum* is not available, boil up a few crystals of $FeSO_4, 7\,H_2O$ in the prepared nitric acid.

Exercise 96.—The metallic substance provided consists of silver alloyed with a small proportion of copper. Find the percentage of silver in it by Volhard's method.

Directions.—Dissolve about 0.5 grm. of the alloy in HNO_3; boil for two or three minutes to remove any nitrous acid produced; cool and make up to 100 cu. cm. Proceed as directed in Ex. 94. Ignore the presence of copper nitrate.

USE OF SODIUM SULPHIDE (Na_2S)

In alkaline solutions this compound precipitates the metals zinc, cadmium, nickel, &c., from solutions of their salts according to the equation—

$$Na_2S + ZnSO_4 = ZnS + Na_2SO_4,$$

so that if the strength of either solution is known we can determine that of the other, providing the end-point can be determined with sufficient accuracy. Since the composition of ordinary commercial sodium sulphide varies, a solution is usually prepared by passing sulphuretted hydrogen into caustic soda ($2\,NaOH + H_2S = Na_2S + 2\,H_2O$), and its strength found by titration againt a suitable standard solution. This is usually one of zinc salt, since standard sulphide is especially used in the estimation of this metal. As the completion of the reaction cannot be observed directly (for the precipitated sulphide does not settle quickly, neither does it show much tendency to clot), the end-point is found by determining when sodium sulphide is present in slight excess from its effect upon some external indicator such as a bright silver coin, or a drop of solution of lead or nickel salt, all of which immediately darken. Sodium nitroprusside similarly becomes purple. Unfortunately the same effects are produced upon the indicator by the zinc sulphide itself; so care must be taken that the suspended solid is removed before the test is made. The method of doing this will be explained in the exercise following. Beginners appear to get better results with the lead indicator than with the others.

For practical purposes it is found convenient to make the solution of sulphide so that 1 cu. cm. = 0.01 grm. zinc.

Exercise 97.—Make some standard sodium sulphide solution of strength 1 cu. cm. = 0·01 grm. zinc.

Directions.—1. *Solution roughly of the required strength.* Dissolve about 4 grm. of 94-per-cent NaOH in a little water, and pass H_2S into it as long as the gas is absorbed. When saturated, the solution should smell strongly. Next, add bench NaOH till, after shaking up, all odour of H_2S has disappeared; then dilute with water to $\frac{1}{2}$ l. and mix thoroughly.

2. *Prepare the following solutions* while the H_2S is being absorbed, and label each one.

(*a*) *Standard Zinc Solution.*—Since 287.55 grm. of zinc sulphate crystals ($ZnSO_4$, $7H_2O$) contain 65.37 grm. of zinc, dissolve up 10.997 grm. to $\frac{1}{4}$ l. in graduated flask. 1 cu. cm. of this solution will contain 0.01 grm. zinc.

(*b*) *Indicator: alkaline solution of lead.*—To a few cubic centimetres of fairly strong solution of sodium tartrate (or tartaric acid neutralized with NaOH) add solution of lead acetate, then NaOH till the white precipitate of lead tartrate dissolves. Apply heat if necessary.

(*c*) *Ammoniacal Solution.*—Mix together about 50 cu. cm. bench ammonium carbonate with about 150 cu. cm. bench AmOH.

3. *Titration.*—Na_2S solution in burette.

(i) To each portion of zinc solution taken add the ammoniacal solution—a few drops at a time—until the precipitate formed redissolves on shaking.

(ii) For the first rough test, run in the Na_2S as long as the precipitate (ZnS) appears to increase; after that about 1 cu. cm. at a time until excess is indicated after being well shaken.

(iii) Test for excess of Na_2S as follows:—

(*a*) Place one drop of indicator near the edge of a filter paper. Withdraw a drop of the turbid liquid on another glass rod, and, holding the paper vertically, apply the drop about 5 mm. below the alkaline moist patch. The ZnS withdrawn with the liquid will then remain where the rod touched the paper, while the liquid will travel upwards to the indicator. The formation of a brown line marks excess of Na_2S. The line is most readily seen when the paper is held up to the light.

Or (*b*) lay a filter paper on a white glazed tile, and damp it with the indicator; then place a drop of the turbid liquid on another filter paper laid momentarily on the first and slightly pressed down by the rod. A brown stain on the *lower* paper marks the presence of Na_2S.

4. *Dilution.*—Probably less than 25 cu. cm. of Na_2S solution will be required for 25 cu. cm. of zinc solution. Suppose 15 cu. cm. are found sufficient; evidently these on dilution to 25 cu. cm. will provide a solution of which 1 cu. cm. = 0.01 grm. zinc.

Note.—Since sodium sulphide solution decomposes on keeping, its value must be redetermined before future use.

Exercise 98.—Assuming that the specimen of sheet brass (English) consists only of copper and zinc, find the percentage of zinc present.

Directions.—1. *Solution of Alloy.*—Dissolve about 1 grm. to a clear blue solution. Use about 5 cu. cm. of concentrated HNO_3. Afterwards add an equal volume of concentrated H_2SO_4, and heat carefully as long as brown fumes are expelled; but do not evaporate to dryness. Allow to become cold, then add 100 cu. cm. to 150 cu. cm. of water. Any white residue should completely dissolve, since English brass contains practically no lead.

2. *Removal of Copper.*—Add a little dilute HCl, and precipitate this metal with H_2S from a hot solution, and filter off. Immediately wash the precipitate and filter paper—once with diluted bench HCl and twice with H_2S water. Add the wash liquids to the filtrate, which should be colourless.

[Treat the copper sulphide as follows in preparation for Ex. 99. Wash it from the paper into a beaker without loss of time; any traces left must be dissolved off in dilute HNO_3. Similarly dissolve the main portion. When cold, make up the solution to 100 cu. cm., and keep in a stoppered bottle till required.]

3. *Preparation of Zinc Solution.* - Boil down the solution

to less than 100 cu. cm. All H_2S should now be expelled. Cool and make up to 100 cu. cm.

4. *Titration with standard* Na_2S.—See Ex. 97. As this solution is acid, rather more Am(OH) will be required to produce and redissolve the precipitate. Much excess, however, must be avoided. *Note.*—Accurate results can only be got by carrying out this titration exactly in the same way as when the sulphide was standardized.

USE OF POTASSIUM CYANIDE IN ESTIMATING COPPER

Parkes's Method. — Though not a precipitation method, this is given here because in many respects it resembles that just used for estimating zinc. The standard cyanide is made up so that 1 cu. cm. = a definite weight of copper, and does not necessarily bear any simple relationship to N. strength. The reacting solutions are both alkaline, but the precipitation of copper hydroxide is prevented by the addition of ammonia—not in too great excess, however, or the results are not concordant. To be trustworthy, the estimation must be carried out in exactly the same way as the standard solution is made. Although the method, at least with a beginner, may not be quite so accurate as that given in Ex. 84, it is of more general application, and is commonly used by analytical chemists.

The addition of ammonia to a solution of copper sulphate first produces a light-blue precipitate which dissolves in excess to a dark-blue solution containing $CuSO_4, 4NH_3, H_2O$. The addition of potassium cyanide destroys this coloured compound, and produces several substances, among them being the double cyanide CuCN, KCN. The quantity of cyanide found necessary to effect this change may thus be used to measure the weight of copper present.

Exercise 99. — Prepare a standard solution of potassium cyanide, so that 1 cu. cm. = 0·005 grm. copper.

Directions.—1. *Rough Solution.*—Dissolve about 20 grm. of the cyanide up to 500 cu. cm.

2. *Standard Solution of Copper.*—Weigh out accurately 2.5 grm. of pure copper (foil or wire will do), and dissolve in about 5 cu. cm. concentrated HNO_3, mixed with an equal volume of water. Evaporate down till most of the acid has been expelled, taking care that there is no loss by spirting. Transfer to a 500-cu.-cm. graduated flask together with rinsings; cool, and make up to the mark. 1 cu. cm. = 0.005 grm. copper.

3. *Standardization of the* KCN.—KCN in burette. To each quantity of copper solution taken (say 25 cu. cm.), add NaOH till all $Cu(OH)_2$ is precipitated, then 1 or 2 cu. cm. of bench ammonia—but always the same definite volume—to produce the deep-blue solution. Run in the KCN till only a faint tint (bluish) remains. Dilute the KCN solution to make it equivalent to that containing the copper. 1 cu. cm. of KCN will now = 0.005 grm. copper. (Whatever average volume of KCN is found necessary to decolorize 25 cu. cm. of copper solution must be diluted to 25 cu. cm., and other volumes in similar proportion.)

Exercise 100. — Estimate the percentage weight of copper in the sample of brass analysed in Ex. 95.

Directions. — Use the solution of copper put by, and titrate it exactly as given in Ex. 99. If this has not been kept, dissolve a fresh portion of the brass, precipitate the copper as sulphide, and follow the treatment given in Ex. 98.

USE OF URANYL ACETATE IN ESTIMATING PHOSPHORIC ACID

Basic salts of uranium contain the radical uranyl, UO_2, the formula for the acetate being $UO_2(CH_3.COO)_2$, $2\,H_2O$. This salt dissolves in water, and can be used to precipitate phosphoric acid in presence of acetic acid as uranyl hydrogen phosphate, UO_2HPO_4. The equation—

$$\underbrace{UO_2(CH_3.COO)_2,\ 2\,H_2O}_{424.6} + \underbrace{NaNH_4HPO_4,\ 4\,H_2O}_{209.2}$$

$$= UO_2HPO_4 + CH_2.COONa + CH_3.COONH_4 + 6H_2O$$

indicates that 424.6 grm. of uranyl acetate = 209.2 grm. of microcosmic salt (or 71 grm. of P_2O_5 when united with alkali). A slight excess of the former salt produces a brown coloration with potassium ferrocyanide. But since the indications may be somewhat modified by the presence of other salts, or, generally speaking, by any difference in character from the solution originally used, it is obviously necessary that all estimations must be carried out as nearly as possible under conditions similar to those of standardization. Points to be borne in mind are (i) that the purity and state of hydration of ordinary commercial phosphates cannot be relied upon; (ii) that solutions standardized against alkaline phosphate can only be used in estimating other alkaline phosphates; for when phosphoric acid is combined in such substances as bone ash or other similar manure, mineral acid is required for its solution, and salts are produced which may seriously interfere with the indications of the ferrocyanide; (iii) that the mineral acid so used must be neutralized by ammonia, or it will prevent the precipitation of the uranyl phosphate; (iv) that any phosphate precipitated by the ammonia may be redissolved in acetic acid in which the uranyl compound is insoluble; and (v) for the estimation of P_2O_5 in bone ash, &c., the uranyl solution must be standardized against tricalcic phosphate, whose percentage purity is usually found by a gravimetric method.

Exercise 101.—Make a standard solution of uranyl acetate, so that 1 cu. cm. = 0·005 grm. P_2O_5.

Directions.—1. *Solution of approximate strength.*—Dissolve about 16 grm. of uranyl acetate crystals in water, add 25 cu. cm. glacial acetic acid, and make up to 500 cu. cm. The acetic acid renders the solution less liable to change under the influence of light. The theoretical weight of the pure salt (14.94 grm.) might be expected to give the required solution; but allowance has to be made for the interfering action of other salts; and the exact relationship between the weights of uranyl salt and phosphate when the end-point is reached (as shown by the indicator) must be determined by a special test. When this is known the uranyl solution may be used to estimate any similar phosphate. Of alkaline phosphates that of most reliable composition is KH_2PO_4 (W. B. Giles), although carefully selected crystals of microcosmic salt are almost as good.

2. *Solution of Microcosmic Salt.* — Since 418.4 grm. contain 142.1 grm. of P_2O_5, 5 grm. of the oxide will be contained in $\frac{418.4}{142.1} \times 5$ grm. of salt. Dissolve $\frac{1}{4}$th of this weight (3.681 grm.) of selected crystals up to 250 cu. cm. 1 cu. cm. = 0.005 grm. P_2O_5.

3. *Titration.* — Uranyl acetate in burette. Boil each quantity of $NaNH_4HPO_4$ solution before adding the uranyl solution. For first rough test run it in as long as the precipitate increases; then add 1 cu. cm. at a time till excess is indicated.

External indicator: a fresh solution of K_4FeCy_6, several drops of which are placed upon a white tile. When excess of uranyl acetate is suspected, apply a drop withdrawn in the usual way. Excess is shown by a faint brown coloration due to uranium ferrocyanide.

4. Label the uranyl solution. Suppose it is found that 23.8 cu. cm. = 25 cu. cm. of the solution of phosphate, evidently 1 cu. cm. = $0.005 \times \frac{250}{238}$ grm. P_2O_5, for use in the estimation of alkali phosphates.

Exercise 102. — By means of the standardized uranyl solution, estimate the percentage weight of Na_2HPO_4 in a laboratory sample. How does it compare with the theoretical value?

Directions.—1. Weigh out 6.3 grm., and dissolve up to 250 cu. cm. A little calculation will show that 1 cu. cm. of this solution should contain 0.005 grm. P_2O_5 if the salt is pure, and that 25 cu. cm. should require the same volume of uranyl solution as used in the last exercise.

2. *Precaution.* — Since ammonium salts are specially active in modifying the colour produced by the $K_4FeC_6N_6$, and ammonium salt was present in the phosphate used to standardize the uranyl acetate, a little ammonium salt must now be specially added, to make the conditions as nearly alike as possible. To each quantity of Na_2HPO_4 solution taken for titration, add 1 cu. cm. of bench AmOH, then acetic acid to neutralize it.

3. Uranyl solution in burette, and follow the directions given in Ex. 101.

Exercise 103. — Assuming that the laboratory sample of tricalcic phosphate is pure, find the percentage of P_2O_5 in some bone ash.

Directions.—1. *Make a Standard Solution of* $Ca_3(PO_4)_2$.—Weigh out accurately 2.73 grm. of dry $Ca_3(PO_4)_2$ into a 250-cu.-cm. graduated flask, and dissolve in as little HCl as possible. Add AmOH in sufficient quantity to neutralize the free mineral acid, and precipitate the $Ca_3(PO_4)_2$; then redissolve in acetic—avoiding much excess in either case. Add water to the mark. A little calculation will show that if the $Ca_3(PO_4)_2$ is pure, the solution will contain 0.005 grm. P_2O_5 per cubic centimetre.

2. *Standardize the uranyl solution* against the calcium phosphate. Uranyl acetate in burette, and follow generally the directions given in Ex. 101. *Note.*—Since boiling is apt to precipitate the $Ca_3(PO_4)_2$, except for the first rough trial, do not apply heat till the precipitation of uranyl phosphate is nearly completed. Label the solution 1 cu. cm. $= x$ grm. P_2O_5 [in $Ca_3(PO_4)_2$]. If you have used pure salts, both your standard solutions of phosphates [$NaNH_4HPO_4$ and $Ca_3(PO_4)_2$] contain 0.005 grm. P_2O_5 per cubic centimetre. Do you find this borne out by the behaviour of your uranyl solution?

3. *Estimate the* P_2O_5 *in the Bone Ash.*—Since this substance contains calcium (and magnesium) phosphate, but no iron nor aluminium, make a solution of 2 to 3 grm. as directed in 1, and make the estimation, observing the precautions given in 2.

CHAPTER X

Miscellaneous Exercises

Exercise 104.—Find the proportion of Na_2O in a sample of borax crystals. How does it agree with the formula of prismatic borax—$Na_2B_4O_7$, $10\,H_2O$?

Directions.—1. Dissolve up about 5 grm. to 250 cu. cm., and titrate with $\frac{N.}{10}$ H_2SO_4.

2. Indicator: methyl orange. The liberated boric acid does not interfere with this indicator.

$$Na_2B_4O_7 + H_2SO_4 + 5\,H_2O = Na_2SO_4 + 4\,H_3BO_3.$$

Exercise 105.—Estimate the percentage weight of B_2O_3 in the same specimen of borax.

Directions.—1. Use same solution as for Ex. 104, and titrate each portion taken with H_2SO_4 till methyl orange shows liquid to be just acid. Boil to expel any CO_2 present; cool, and titrate back with $\frac{N.}{10}$ NaOH till exact neutrality is obtained, as shown by appearance of pure yellow colour. The only free acid now present is boric acid, which does not affect methyl orange.

2. Add at least half the volume of glycerin, one or two drops of phenolphthalein, and titrate with $\frac{N.}{10}$ NaOH till red colour appears.

Note.—R. T. Thomson advocates the use of glycerin to make the phenolphthalein sensitive to boric acid.

Boric acid reacts with NaOH as shown—

$$NaOH + H_3BO_3 = NaH_2BO_3 + H_2O,$$

so that 80 grm. NaOH = 70 grm. B_2O_3.

Exercise 106.—Estimate the percentage of $CaCO_3$ in some impure calcite, assuming that no other carbonate is present.

Directions.—See Ex. 40. Neglect the slight amount of insoluble matter.

Exercise 107.—Determine the solubility of oxalic acid in water at the temperature of the laboratory, which should be stated.

Directions.—1. Saturate about 50 cu. cm. of warm water with pure powdered acid, and allow to cool to temperature of laboratory. Some crystals should remain undissolved.

2. Make up 25 cu. cm. of the clear solution to 250 cu. cm., and titrate with $\frac{N.}{10}$ alkali or $\frac{N.}{10}$ $KMnO_4$.

Note.—1 l. should contain about 9.3 grm. of $(COOH)_2$ at 15° to 16°.

Exercise 108.—Make 250 cu. cm. each of $\frac{N.}{10}$ NaOH and $\frac{N.}{10}$ $KMnO_4$. Standardize each with oxalic acid, pure crystals of which are provided.

Exercise 109.—A given powder consists of a mixture of oxalic acid ($H_2C_2O_4$, $2\,H_2O$) and potassium oxalate ($K_2C_2O_4$, $2\,H_2O$). Find the proportion of each present.

Directions.—1. Estimate free oxalic acid with standard alkali. See Ex. 54.

2. Estimate total oxalate with standard $KMnO_4$. See Exs. 61 and 62.

3. Weight of potassium salt will be $\frac{226}{126}$ that of the combined acid.

Exercise 110.—A solution of hydrochloric acid has been partially neutralized by potash. Find the weight of each originally used per litre.

Directions.—1. Total chlorine, and hence total HCl used, obtained by titration with standard $AgNO_3$.

2. Estimate free HCl with standard alkali.

3. Calculate the weight of KOH equivalent to the HCl neutralized.

Exercise 111.—A solution of caustic potash has been partly neutralized with hydrochloric acid. Find the weight of KOH per litre originally present.

Directions.—1. Estimate the free alkali with standard acid.

2. Estimate chlorine, acidifying (or neutralizing) each portion titrated with HNO_3.

Total KOH will be the sum of that found free and that equivalent to the chlorine.

Exercise 112.—Solutions of potassium chloride and potassium bicarbonate have been mixed. Find the weight of each in 1 l.

Exercise 113.—A solution contains both hydrochloric and sulphuric acids. Find the weight of each present per litre.

Directions.—1. Find total acid-forming hydrogen with standard alkali.

2. Find that hydrogen combined with chlorine with standard $AgNO_3$.

Note.—Consider whether there is any advantage in using the portions titrated in (1) for titration with $AgNO_3$ in (2).

Exercise 114.—Find the percentage of available chlorine in some fresh bleaching powder by its oxidizing action on a ferrous salt.

Directions.—1. To about 10 grm. of Mohr's salt (ferrous ammonium sulphate crystals) add about 25 cu. cm. dilute H_2SO_4; dissolve, and make up to 250 cu. cm. with boiled-out water.

2. Prepare solution of bleaching powder. (See Ex. 81.) Dissolve up 1 to 2 grm. of the powder to 250 cu. cm. of solution, and titrate as soon as possible.

3. To 25 cu. cm. of the acid ferrous solution add 25 cu. cm. of the bleaching solution and mix well; then find excess of ferrous iron.

Equation—

$$Ca(OCl_2) + 4\,FeSO_4 + 2\,H_2SO_4 = 2\,Fe_2(SO_4)_3 + CaCl_2 + 2\,H_2O$$

shows 56 grm. of ferrous iron are oxidized by 8 grm. of oxygen = 35.5 grm. available chlorine.

Exercise 115.—Estimate the percentage of barium in some pure crystals of barium chloride. How does it accord with the formula $BaCl_2, 2\,H_2O$?

Method I.—By standard Na_2CO_3. See Exs. 39 and 40. The solution should be neutral.

Method II.—By standard $K_2Cr_2O_7$.

Directions.—The solution of $BaCl_2$ must be made alkaline with AmOH, free from carbonate, and heated to 70° C. Titrate with standard $K_2Cr_2O_7$. The end-point is reached when no further cloudiness is produced, and the clear liquid shows a trace of yellow colour due to slight excess of $K_2Cr_2O_7$. Equation—

$$\underbrace{2\,BaCl_2}_{416.6} + \underbrace{K_2Cr_2O_7}_{294.2} + 2\,NH_3 + H_2O$$
$$= 2\,BaCrO_4 + 2\,KCl + 2NH_4Cl$$

shows relationship between the reacting masses of barium salt and dichromate.

N.B.—It should be noticed that 1 l. of $\frac{N.}{10}$ $K_2Cr_2O_7$, as used in the above or similar estimations, must contain 7.355 grm. $K_2Cr_2O_7$.

Exercise 116.—Estimate the percentage of lead in some "white lead".

Directions.—Dissolve 1 to 2 grm. in acetic acid, and precipitate the lead by a known volume of standard $K_2Cr_2O_7$ taken in good excess. Boil, filter off precipitate, and at once wash well with hot water. Determine excess of $K_2Cr_2O_7$ in filtrate and washings by adding excess of KI, then titrating with $\frac{N.}{10}$ $Na_2S_2O_3$. See Ex. 79.

294.2 grm. of $K_2Cr_2O_7$ = 414.2 grm. Pb; and equations given in Ex. 78 and 79 show relationship between iodine set free and $K_2Cr_2O_7$, &c.

Exercise 117.—Find the weight of NaOCl dissolved in 1 l. of the hypochlorite solution given.

Directions.—Use standard As_4O_6. See Ex. 86.

Exercise 118.—The organic acid provided reduces potassium permanganate. Find its equivalent both as acid and reducing agent.

Directions.—See "Equivalent of Organic Acids", p. 69, also Ex. 53, &c.

Exercise 119.—**A solution contains both sulphuric and oxalic acids. Find the weight of each present in 1 l.**

Directions.—1. Find the total alkali necessary to neutralize both acids.

2. Find weight of oxalic with standard $KMnO_4$, and calculate that of alkali used to neutralize this acid.

3. Difference between results of (1) and (2) will be the equivalent of the sulphuric acid present.

Exercise 120.—**Some sulphuric acid had half its equivalent of potassium hydroxide added to it, together with a small quantity of oxalic acid crystals ($H_2C_2O_4$, $2H_2O$). The solution was made up to $2\frac{1}{2}$ l. Find the weight of each reagent originally used. Solid potassium permanganate and $\frac{N.}{10}$ KOH are provided.**

Exercise 121.—**Find the equivalent of mercury in mercuric compounds by making use of the reaction between mercuric chloride and sodium hydroxide.**

Directions.—Dissolve 2 to 3 grm. of pure $HgCl_2$. Precipitate HgO with N. NaOH used in good excess. Find excess of NaOH with $\frac{N.}{10}$ HCl. The gramme-equivalent of mercury is that weight corresponding to 40 grm. NaOH.

$$HgCl_2 + 2\,NaOH = HgO + 2\,NaCl + H_2O.$$

Exercise 122.—**See if the result obtained in Ex. 121 is confirmed by titrating a solution of mercuric chloride with standard $AgNO_3$.**

Exercise 123.—**Find the proportion in which mercuric chloride and potassium iodide react to form the compound HgI_2, 2 KI.**

Directions.—1. Prepare solutions from the purest salts obtainable: $\frac{N.}{10}$ KI; $\frac{N.}{20}$ $HgCl_2$.

2. $HgCl_2$ solution in burette. First trace of permanent red colour (HgI_2) shows end-point; as any excess of $HgCl_2$ after all the KI has entered into the compound at once decomposes the latter, according to the equation—

$$HgCl_2 + HgI_2, 2\,KI = 2\,HgI_2 + 2\,KCl.$$

Note.—Personne uses this method to estimate mercury.

Exercise 124.—A given solution contains ferrous oxalate and oxalic acid. Find the weight of each present per litre. You are provided with solid potassium permanganate and $\frac{N.}{10}$ alkali.

Directions.—Use the alkali to estimate the free oxalic acid; and $\frac{N.}{10}$ $KMnO_4$ to estimate total oxalate.

Calculate the weight of $KMnO_4$ used by the free oxalic acid. The remainder has reacted with ferrous oxalate according to the equation

$$\underbrace{6\,KMnO_4}_{948} + \underbrace{10\,Fe(COO)_2}_{1438} + 24\,H_2SO_4$$
$$= 5\,Fe_2(SO_4)_3 + 3\,K_2SO_4 + 6\,MnSO_4 + 24\,H_2O.$$

Exercise 125.—Estimate the percentage of sodium nitrite in the sample provided by making use of its reducing action towards potassium permanganate.

Directions.—1. Weigh out about a gramme of the nitrite from a weighing-bottle, and dissolve up to 100 cu. cm.

2. Prepare some $\frac{N.}{50}$ $KMnO_4$.

3. Mix together 10 cu. cm. nitrite solution with 200 cu. cm. of the $KMnO_4$ solution, and add about 5 cu. cm. dilute H_2SO_4. Warm to 40°, and allow a few minutes for the reaction to become complete. *Note.*—The reaction takes place very slowly in cold solution.

4. Find excess of $KMnO_4$ with $\frac{N.}{10}$ oxalic acid. The

proportion between the nitrite and the $KMnO_4$ reduced by it is shown in the equation

$$2\,KMnO_4 + 5\,NaNO_2 + 3\,H_2SO_4 \\ = K_2SO_4 + 2\,MnSO_4 + 5\,NaNO_3 + 3\,H_2O.$$

What objections are there to titrating the warmed nitrite directly with $KMnO_4$?

Exercise 126.—Estimate the percentage of pure tin in a commercial sample.

Directions (Löwenthal's Method).—1. Dissolve about 0.5 grm. of the tin in 5 cu. cm. concentrated solution of ferric chloride containing a little free HCl. The tin is present as chloride, and has reduced its equivalent of ferric to ferrous iron. Use a 250-cu.-cm. flask, and prevent oxidation by adding a pinch of $NaHCO_3$ to expel air. Warm gently till the solution is complete; then cool, and add cold boiled-out water up to the mark.

2. Estimate the ferrous iron with $\frac{N.}{10}$ $KMnO_4$. Equation $SnCl_2 + Fe_2Cl_6 = 2\,FeCl_2 + SnCl_4$ shows that 2×55.8 grm. $Fe'' = 119$ grm. Sn. (See also Ex. 129, and Precautions in using Permanganate, p. 75.)

Exercise 127.—Assuming that no iron is present, estimate the percentage of metallic zinc in zinc dust.

Directions.—1. Weigh out accurately about 3 grm. of iodine into a small strong bottle fitted with a glass stopper, and dissolve in water with the aid of KI.

2. Add about 0.5 grm. of the zinc dust, ground very finely, and accurately weighed.

3. Tie down the stopper securely, and place the bottle in a water-bath, kept near boiling-point, for one hour. Occasionally shake up the contents of the bottle. By this time the metallic zinc will have formed ZnI_2. The oxide of zinc will remain unacted upon.

4. Allow the bottle to cool; transfer its contents with the rinsings to a 200-cu.-cm. graduated flask, and add water to the mark. Find the excess of iodine with standard $Na_2S_2O_3$.

The weight of metallic zinc in the dust taken was $\frac{65.5}{254}$ that of the iodine used up.

Exercise 128.—Repeat the estimation carried out in Ex. 127, using a gasometric method.

Directions.—Find the volume of the hydrogen evolved when 0.5 to 0.75 grm. of the zinc dust is treated with sulphuric acid. (See apparatus used for determining equivalents of metals.) Reduce volume of hydrogen to S.T.P.

Remember that 22.4 l. of hydrogen (at S.T.P.) are evolved by action of 65.4 grm. of zinc.

Exercise 129.—Estimate the proportion of metallic iron in some "reduced iron" (ferrum redactum).

Method (*A*). *Directions.*—1. Dissolve about 2.5 grm. of $HgCl_2$ in 50 cu. cm. of water contained in a glass-stoppered bottle. Add about 0.5 grm. of the iron powder accurately weighed out; then digest for one hour (at least), as given in (3) of exercise 127. Iron oxide is unacted upon.

2. Make a solution of $MnSO_4$: 10 grm. of crystals dissolved up to 50 cu. cm. roughly.

3. Cool the contents of the bottle, and filter quickly into 100-cu.-cm. graduated flask. Wash out bottle with boiled-out water, allowing the rinsings to pass into the flask. Make up to the mark with boiled-out water; and proceed to titrate the ferrous solution at once.

4. To each 10 cu. cm. add 10 cu. cm. (about) of dilute H_2SO_4, and the same quantity of $MnSO_4$ solution, and titrate with $\frac{N.}{10}$ $KMnO_4$.

Note.—The $KMnO_4$ should be dropped in slowly. The end-point colour is not of the same tint as when no $MnSO_4$ is used. Of what use is this salt?

Method (*B*). *Directions.*—1. Make a hot (short of boiling) solution of (roughly) 5 grm. of $CuSO_4$, 5 H_2O in 75 cu. cm. water contained in a small flask—preferably stoppered. Add 0.5 to 1.0 grm. of the iron powder accurately weighed. Stand for about 15 minutes with occasional shaking. Keep out air as much as possible.

2. Quickly filter off the precipitated copper, &c. (iron oxide is acted upon) into 100-cu.-cm. measuring-flask. Rinse out with boiled-out water, and pass into the flask. Make up to the mark, when cold, with dilute H_2SO_4.

3. Titrate the ferrous solution with $\frac{N.}{10}$ $K_2Cr_2O_7$.

Exercise 130.—Repeat the estimation of metallic iron in "reduced iron" by a gasometric method.

Directions.—See Ex. 128.

CHAPTER XI

Notes on Electrolytic Dissociation and Indicators

When an electric current passes through certain solutions, especially when water is the solvent, the substance dissolved gradually separates into two portions with unlike chemical properties. One portion gathers round the positive terminal and the other round the negative. Solutions of compounds which behave in this way are called "electrolytes"; and since the disrupted components appear to move through the solution (to one or other terminal or "electrode") they were called by Faraday "ions" (εἶμι = to go). Metals, ammonium, and the acid-forming hydrogen of acids make their appearance at the "cathode" and are referred to as "kations", while those constituents found at the "anode" are known as "anions".

This behaviour may be explained by supposing that the ions resulting from each molecule are oppositely electrically charged. When the oppositely electrified terminals of a battery are introduced into the solution, the positively charged ions (kations) are consequently attracted to one terminal—the kathode—and repelled from the other—the anode; whilst those negatively charged (anions) are attracted to the anode and repelled from the kathode. Contact with the electrodes neutralizes the attracted ions; they are "ions" no longer. The conductivity of a solution thus appears to depend upon the number of ions it contains; and this number will vary with the quantity of substance dissolved, and with the readiness with which its molecules electrolytically dissociate (or ionise).

Normal salt solutions, and those of certain acids and bases, conduct the electric current most readily; from which it must be assumed that these contain the greatest proportion of dissociated molecules. Such acids and bases are called "strong", and the common mineral acids and caustic soda and potash serve as examples. There is evidence that most of the ordinary bench reagents contain considerably more than half their molecules in the ionized state. But whether the electrolyte be a good or poor conductor, i.e. whether it may be designated "strong" or "weak", the proportion of its dissociated molecules increases with dilution until all assume this condition. Even water itself, from the fact that it conducts the electric current, though very feebly, must be looked upon as containing at least some of its molecules in a dissociated state.

From this point of view chemical reactions are explained as due to reactions between the ions, which when removed from solution are replaced by others derived from previously undissociated molecules, until one of the reagents is exhausted. It is usual to distingush kations by dots and anions by dashes—the number of dots and dashes corresponding with the valency. The ions provided by sodium hydroxide are represented as $Na^{\cdot}$ and OH'; and those of hydrogen sulphate as $2\,H^{\cdot}$ and SO_4''. The neutralization of caustic soda by hydrochloric acid, since both are "strong", may be represented thus—

$$H^{\cdot} + Cl' + Na^{\cdot} + OH' = Na^{\cdot} + Cl' + H_2O.$$

One of the products—being a normal salt and remaining in solution—is represented in the dissociated state; but the other product—water—whose tendency to dissociate is so small, is represented as a molecule. Weak bases and weak acids are also similarly represented, although their tendency to dissociate is much greater than water.

The ion common to all dissociated acids is hydrion ($H^{\cdot}$), and to it their acid properties are ascribed. Similarly, hydroxidion $(OH)'$ is common to all dissociated alkalis, and is responsible for their alkalinity. Neutralization is theoretically attained when acid and alkali have been mixed so as to produce equivalent quantities of hydrions and hydroxidions; for the small proportion of ions which do not unite to form water molecules is probably no greater than the water itself contained. We should consequently expect an aqueous solution of a normal salt also to be neutral, since none of its ions consist either of hydrion or hydroxidion. This is only true of those normal salts resulting from reactions between strong acids and strong bases; such as, sodium chloride, potassium sulphate, &c. Where a weak acid or weak base takes part in their formation, solutions showing distinct acidity or alkalinity are obtained. Suppose the acid is weak. Solution dissociates more or less of the salt, and produces momentarily, we may suppose, an equivalent number of kations and anions; but the tendency of the acid to ionize being small, its anions largely unite with hydrions derived from the water, and become molecules of acid. The base, however, being strong, comparatively few molecules form; and, as a result, a sufficient excess of hydroxidions (also derived from water) remains to affect the indicator. Potassium cyanide serves as an example of this behaviour. The molecule ionizes into $K^{\cdot}$ and CN' when the anion combines with $H^{\cdot}$ (derived from the water) to form molecules of HCN. The OH'—also derived from the water—is responsible for the alkaline reaction. Borax and, to a lesser extent, sodium acetate behave similarly.

Normal sodium phosphate, although derived from a strong base and moderately strong acid, appears to behave exceptionally as its solution is strongly alkaline. An explanation is afforded by regarding the salt as derived from the strong base caustic soda and a weak acid, HNa_2PO_4.

INDICATORS USED IN ACIDIMETRY AND ALKALIMETRY

According to the above hypothesis, indicators oi acids and alkalis must possess a weakly acid or basic character themselves, and show slight tendency to dissociate, although their salts may do so comparatively freely. Their marked colour-changes are due to differences in colour between their undissociated molecules and ions derived from them. The addition of fairly strong acid, or comparative abundance of hydrogen ions, furnishes a far greater opportunity than existed previously for what anions of the indicator are present to meet hydrions and thereby form acid molecules. Whatever proportion of molecules of the indicator was previously dissociated, it is now much smaller, and any colour exhibited will be due to these molecules. On the other hand, the introduction of a strong base, or abundance of hydroxidions, lessens the proportion of hydrions through the formation of water molecules (whose tendency to dissociate is extremely slight); and whatever colour is now seen is due to anions of the indicator.

Although the composition of many indicators is unknown, that of one of the commonest is well established, and may be used to illustrate the application of the hypothesis. Phenolphthalein possesses the properties of a very weak acid, and its solution in water or in the presence of acid is colourless. Its molecules are therefore assumed to be colourless. With alkalis it forms salts whose solutions are red. This colour must be due to anions of phenolphthalein, for other salts of alkalis are usually colourless.

The composition of litmus is unknown: but if we may apply an explanation of its behaviour similar to the above, red is the colour of its molecules, and blue that of its anions; and since its neutral solution is purple, we must assume that a considerable proportion of its molecules are dissociated to provide sufficient anions to modify the red due to the undissociated molecules. Litmus thus appears to dissociate more freely than phenolphthalein; or, in other words, to possess a somewhat stronger acid character. It will thus be seen that although the indicators used in acidimetry and alkalimetry show small tendency to dissociate, there is considerable difference between them in this respect; and in making a selection, the character of the acid or alkali to be titrated must be taken into account. For instance, an indicator comparable in strength with the acid used in a titration will require too great an excess of acid to overcome the tendency of the indicator to dissociate and cause the disappearance of any colour due to its anions. Again, a very weak acid indicator used with a weak base will produce a salt which can be hydrolysed by water; and its small amount of ionization will be masked by its acid *molecules* in spite of a fair excess of base. This is seen to occur when phenolphthalein is used in titrating ammonia. Strong acids like picric acid, although coloured, are useless as indicators; for their dissociation is so great that the colour seen is due to their anions, just as when their salts dissociate.

Many chemists, however—notably Hantzsch—do not accept the explanation of the behaviour of indicators as due to dissociation. They consider the changes in colour to be due to rearrangements of the atoms within the molecules.

Phenolphthalein results when phenol and the anhydride of phthalic acid are gently heated with strong sulphuric acid. Its composition is well known. For use as an indicator it is generally dissolved in alcohol. The solution is colourless, and shows no change when mixed with water or acid, but sharply becomes red when the slightest trace of alkali is added. It is an excellent indicator for estimating the weaker acids —especially organic—when titrated with caustic soda or potash; but it is useless if the acid is *very* weak, for then the salt formed with the indicator will dissociate and show a pink colour—due to its anions—before the acid being titrated is neutralized. Neither may it be used with ammonia or other weak bases, nor in the presence of compounds of ammonia, as under these circumstances the colour-change is not sharp, and too great excess of base is required.

Normal carbonates of alkalis produce the same red colour as the alkalis themselves, but acid carbonates do not. The point when the former are wholly converted into the latter may be thus readily determined. This is supposed to be due to dissociation of the normal salt, which in the presence of water becomes free alkali and acid salt. The acid salt dissociates scarcely at all. Since the decomposition of a carbonate charges the solution with carbonic acid, which is more prone to dissociate than the indicator, the carbon dioxide must be boiled out before assuming that the reaction is complete. The disappearance of the red colour on standing may be due to absorption of carbon dioxide from the air; or, as Sutton suggests, because the tendency of the indicator salt to ionize is gradually overcome by its tendency to react with water when acid molecules are again formed.

Litmus.—As a general indicator for strong inorganic acids and bases, litmus is best known and most generally useful; but for the titration of weak acids or bases its indications are unreliable. Amongst the weak acids must be included phosphoric, arsenic, and sulphurous acids. It is an aqueous solution of colouring matter extracted from certain lichens. Litmus test-paper is prepared by soaking paper in the solution made weakly acid, alkaline, or neutral. That made with glazed paper is most sensitive. As in the case of phenolphthalein, so with litmus: carbon dioxide set free during a titration must be expelled before assuming that the end-point of the reaction is reached.

Methyl orange or *Tropæolin D* is the sodium salt of the sulphonic acid of an azo dye. Its behaviour suggests that its acid is considerably stronger than those contained in phenolphthalein and litmus. Orange-coloured in the solid state, it dissolves to a yellow solution in water, and turns red on acidifying. It is an excellent indicator in alkalimetry, being thoroughly reliable even when weak bases are titrated; but it is useless for estimating organic or other weak acids. The fact that its colour is uninfluenced by carbonic acid makes it specially useful in titrations where carbon dioxide is liberated, as boiling off becomes unnecessary. Boric acid, too, makes no difference to its colour; hence it can be used in the titration of borax with mineral acid. The colour-change is best followed when the tint is light.

The behaviour of methyl orange may be thus explained: the acid being moderately strong, its sodium salt dissociates, and the yellow colour is due to its anions. The same colour is seen when the acid itself is dissolved, and points to a considerable dissociation of its molecules. The pink colour due to these does not appear until a sufficient quantity of hydrions has been introduced to overcome this ionizing tendency. Hence its uselessness for the titration of weak acids. A buff colour suggests a mixture of molecules and anions. The tendency of methyl orange to dissociate is too great to be affected by many organic acids and some inorganic acids—notably carbonic and boric;

and excess of either of these gives no indication of its presence.

Turmeric, which is seldom used in volumetric work, is obtained from the dried rhizome of an Eastern plant much used as an ingredient of curry. The yellow solution is an alcoholic extract of that colouring matter remaining after extraction with water. Alkalis change the yellow to brown. It is commonly used in the form of "turmeric paper", which is prepared in a similar way to litmus paper, and is chiefly useful for the detection of boric acid. Alkali in the presence of coloured matter may also be detected by it. The paper should be kept in the dark, as it bleaches in daylight.

SOME OTHER INDICATORS

Potassium Chromate (K_2CrO_4).—The use of this salt as an indicator depends upon the fact that red silver chromate cannot exist in contact with solutions of halides of metals.

$$\begin{aligned} & 2\,Na^{\cdot} + 2\,Cl' + Ag_2CrO_4 \\ & \qquad = 2\,AgCl + 2\,Na^{\cdot} + CrO_4''. \end{aligned}$$

The end-point of a reaction between silver nitrate and a haloid salt is more sharply defined by the appearance of silver chromate than by its disappearance. Hence the silver nitrate should be added to the solution of haloid salt containing a small quantity of potassium chromate rather than the other way about.

Starch is a valuable indicator in reactions involving the use of iodine. It should be used as a very dilute solution in water, and should be freshly made unless a few drops of chloroform or solution of mercuric chloride have been added to preserve it. It should give the well-known deep-blue colour with iodine. If shades of brown or green appear instead, its indications must not be relied upon. One cu. cm. of the solution, prepared as directed in Exercise 16, will be quite sufficient for each titration. The blue substance called "iodide of starch" is immediately affected by sodium thiosulphate, even in traces. By some chemists it is regarded as a true chemical compound; by others, as a solution of iodine in the starch. It is important to remember the effect of heat on this indicator, since the disappearance of its blue colour in the titrations is taken to indicate excess of the reagent. The colour is also destroyed by the presence of much free chlorine.

Iodized starch paper is usually white filter-paper which has been soaked in a solution of starch and potassium iodide. After drying, it is cut into strips and preserved in stoppered bottles. Before being used for testing, it should be moistened with water to render it more sensitive. It is useful for detecting those substances which decompose potassium iodide, such as ozone, chlorine, &c. [The effect of much excess of chlorine must be borne in mind.] The liberated iodine immediately forms the blue iodide of starch. The particular substance reacting with the iodide may be distinguished by the other compounds produced. Thus ozone makes the paper alkaline from the production of potash.

$$O_3 + 2\,K^{\cdot} + 2\,I' + H_2O$$
$$= O_2 + 2\,K^{\cdot} + 2\,OH' + 2\,I,$$

or as commonly written—

$$O_3 + 2\,KI + H_2O = O_2 + 2\,KOH + 2\,I.$$

Chlorine simply replaces the iodine, and solutions of the unstable hypochlorites act similarly.

Potassium ferricyanide [$K_3Fe(CN)_6$] yields with ferrous sulphate an intensely blue precipitate of ferrous ferricyanide, $Fe_3 2[Fe(CN)_6]$, known as Turnbull's blue.

$$3\,FeSO_4 + 2\,K_3Fe(CN)_6 = Fe_3\,2\,[Fe(CN)_6] + 3\,K_2SO_4.$$

With ferric chloride it gives no precipitate at all, but merely a dirty-brown solution, whilst potassium dichromate appears practically unaltered. Hence as long as any of the ferrous compound remains in the mixed liquids, the drop reagent will show a blue colour, which becomes less in intensity as the ferrous constituent decreases, and disappears with its complete oxidation. Solution of potassium ferricyanide must be freshly made for each test, as the salt quickly changes. Among other causes of this change are light, sulphuretted hydrogen and ammonia, which reduce ferricyanide to ferrocyanide and other substances. And it must not be forgotten that ferrocyanide yields a dark-blue precipitate (or colour) of Prussian blue—$Fe_4 3[Fe(CN)_6]$—with ferric salts.

$$3\,K_4Fe(CN)_6 + 4\,FeCl_3 = Fe_4 3[Fe(CN)_6] + 12\,KCl.$$

The use of other substances as indicators, such as *potassium ferrocyanide* in estimating phosphoric acid, *iron alum* in estimating silver with thiocyanate, and alkaline solution of *lead* in estimating zinc, has been explained in the exercises.

TABLE OF STANDARD SOLUTIONS IN COMMON USE

A *standard solution* may be of any possible strength; but its value in some special reaction must be known accurately. Some standard solutions are termed *normal*, *decinormal*, and so on; others, which bear no simple relationship to these values, are often referred to as *empirical.*

The "strength of a solution" is commonly given as the weight of its solute in 1 cu. cm.; but it may also express the weight in 1 cu. cm. of some constituent given up during a reaction; or the equivalent weight of some other substance with which 1 cu. cm. of the solution reacts. Examples of each will be found in the summarized list following.

Normal solutions, and those simply related to normal strength, are usually indicated by the abbreviations N. (normal), $\frac{N.}{2}$ (seminormal), $\frac{N.}{10}$ (decinormal), 2 N. (twice normal), and so on.

N. caustic soda contains the gramme formula weight (40.008 grm.) of NaOH, and consequently the gramme-equivalent of hydroxyl, per litre.

1 cu. cm. = 0.04 grm. NaOH.

$\frac{N.}{10}$ *caustic soda* contains 4.0001 grm. per litre.

1 cu. cm. = 0.004 grm. NaOH.

N. caustic potash contains the gramme formula weight (50.108 grm.) of KOH per litre.

1 cu. cm. = 0.05611 grm. KOH.

N. sodium carbonate contains half the gramme formula weight (53 grm.) of Na_2CO_3 per litre.

1 cu. cm. = 0.053 grm. Na_2CO_3.

N. sodium bicarbonate contains the gramme formula weight (84.008 grm.) $NaHCO_3$ per litre.

1 cu. cm. = 0.084 grm. $NaHCO_3$.

$\frac{N.}{25}$ *calcium hydroxide* ("lime-water") contains $\frac{1}{50}$ the gramme formula weight of $Ca(OH)_2$ per litre.

1 cu. cm. = 0.001482 grm. $Ca(OH)_2$.

Note.—Although water can dissolve less than 2 grm. of $Ca(OH)_2$ per litre, the addition of sugar enables it to dissolve much more.

$\frac{N.}{10}$ *barium hydroxide* ("baryta water") contains $\frac{1}{20}$ the gramme formula weight of $Ba(OH)_2$ per litre.

1 cu. cm. = 0.00857 grm. $Ba(OH)_2$.

N. ammonia contains 1 mol of NH_3 per litre.

1 cu. cm. = 0.017034 grm. NH_3.

N. hydrochloric acid contains 1 mol (36.468 grm.) HCl per litre.

1 cu. cm. = 0.03647 grm. HCl.

N. nitric acid contains the gramme formula weight (63.018 grm.) HNO_3 per litre.

1 cu. cm. = 0.06302 grm. HNO_3

N. sulphuric acid contains half the gramme formula weight (49.043 grm.) H_2SO_4 per litre. (This weight contains 1 grm. equivalent of acid-forming hydrogen.)

1 cu. cm. = 0.04904 grm. H_2SO_4.

N. acetic acid contains 1 mol (60.032 grm.) $CH_3.COOH$ per litre. (This contains only 1 grm. equivalent of *acid-forming* hydrogen.)

1 cu. cm. 0.06003 grm. $CH_3.COOH$.

N. oxalic acid (when used for its *acid* property) contains half the gramme formula weight (45.008 grm.) of anhydrous acid (or 63.024 grm.) of crystals per litre.

1 cu. cm. = 0.04501 grm. $(COOH)_2$.

N.B.—The above statement holds good also when oxalic acid is used as a *reducing agent*, as in its reaction with $KMnO_4$.

N. acid potassium oxalate (when used for its *acid* property) contains the gramme formula weight of the salt per litre, as this weight contains the gramme-equivalent of acid-forming hydrogen.

1 cu. cm. = 0.12811 grm. C_2O_4HK.

N.B.—When used as a *reducing agent*—

1 cu. cm. = 0.00641 grm. C_2O_4HK.

Remember 1 cu. cm. N. acid = 1 cu. cm. N. alkali.

$\frac{N.}{10}$ *potassium permanganate* contains 3.1606 grm. of $KMnO_4$ per litre, since this weight yields 0.8 grm. of oxygen for oxidizing purposes.

1 cu. cm. = 0.00316 grm. $KMnO_4$.
1 cu. cm. = 0.0008 grm. oxygen.
1 cu. cm. = 0.00558 grm. Fe″.

$\frac{N.}{10}$ *potassium dichromate* contains 4.903 grm. of $K_2Cr_2O_7$ per litre, since this weight yields 0.8 grm. of oxygen for oxidizing purposes.

1 cu. cm. = 0.0049 grm. $K_2Cr_2O_7$.
1 cu. cm. = 0.0008 grm. oxygen.
1 cu. cm. = 0.00558 grm. Fe″.

N.B.—When used in the estimation of barium or lead, $\frac{N.}{10}$ $K_2Cr_2O_7$ then contains one-fortieth of the gramme formula weight of the salt per litre (7·355 grm.).

1 cu. cm. = 0.00736 grm. $K_2Cr_2O_7$.

$\frac{N.}{10}$ *sodium chloride* contains one-tenth of the gramme formula weight (5.846 grm.) of NaCl per litre.

1 cu. cm. = 0.00585 grm. NaCl.
1 cu. cm. = 0.00355 grm. Cl.
1 cu. cm. = 0.01699 grm. Ag.

$\frac{N.}{10}$ *silver nitrate* contains one-tenth of the gramme formula weight (16.989 grm.) of $AgNO_3$ per litre.

1 cu. cm. = 0.01699 grm. $AgNO_3$.
1 cu. cm. = 0.01079 grm. Ag.
1 cu. cm. = 0.00355 grm. Cl.

$\frac{N.}{10}$ *iodine* contains one-tenth of the gramme-equivalent (12.692 grm.) of iodine per litre.

1 cu. cm. = 0.01269 grm. I.

$\frac{N.}{10}$ *sodium thiosulphate*, when used to react with iodine, contains one-tenth of the gramme formula weight (24.822 grm.) of the crystals $Na_2S_2O_3$, 5 H_2O per litre, since this is equivalent to 12.692 grm. of iodine.

1 cu. cm. = 0.02482 grm. $Na_2S_2O_3$, 5 H_2O.
1 cu. cm. = 0.01581 grm. $Na_2S_2O_3$.
1 cu. cm. = 0.01269 grm. I.

$\frac{N.}{10}$ *arsenious oxide* contains one-eightieth of the mol (4.948 grm.) of As_4O_6 per litre, as this is equivalent to 12.692 grm. of iodine.

1 cu. cm. = 0.00495 grm. As_4O_6.
1 cu. cm. = 0.01269 grm. I.

$\frac{N.}{10}$ *potassium thiocyanate* contains one-tenth of the gramme formula weight (9.72 grm.) of KCNS per litre.

1 cu. cm. = 0.00972 grm. KCNS.
1 cu. cm. = 0.01079 grm. Ag.

Standard sodium sulphide is usually made so that—

1 cu. cm. = 0.01 grm. Zn.

Standard potassium cyanide is usually made so that—

1 cu. cm. = 0.005 grm. Cu.

Standard uranyl acetate is usually made so that—

1 cu. cm. = 0.005 grm. P_2O_5.

INTERNATIONAL ATOMIC WEIGHTS
(1917)

Aluminium	Al	27.1	Iron	Fe	55.84
Antimony	Sb	120.2	Lead	Pb	207.20
Arsenic	As	74.96	Magnesium	Mg	24.32
Barium	Ba	137.37	Manganese	Mn	54.93
Bismuth	Bi	208.0	Mercury	Hg	200.6
Boron	B	11.0	Nickel	Ni	58.68
Bromine	Br	79.92	Nitrogen	N	14.01
Cadmium	Cd	112.40	*Oxygen*	O	16.0
Calcium	Ca	40.07	Phosphorus	P	31.04
Carbon	C	12.00	Platinum	Pt	195.2
Chlorine	Cl	35.46	Potassium	K	39.10
Chromium	Cr	52.0	Silicon	Si	28.3
Cobalt	Co	58.97	Silver	Ag	107.88
Copper	Cu	63.57	Sodium	Na	23.00
Fluorine	F	19.0	Strontium	Sr	87.63
Gold	Au	197.2	Sulphur	S	32.06
Hydrogen	H	1.008	Tin	Sn	118.7
Iodine	I	126.92	Zinc	Zn	65.37

NOTES ON THE EXERCISES

Exercise 16.—The blue colour of "iodide of starch" will disappear near boiling-point but reappear on cooling. If the solution of iodine has been rendered quite colourless by the addition of $Na_2S_2O_3$, probably no trace of free iodine is left; and, consequently, no iodide of starch will be formed. The formation of a blue colour, therefore, indicates the presence of free iodine, and the end-point of the reaction is not reached.

Exercise 17.—Strong chlorine water destroys the blue colour first produced. But if the colour appears *at all*, it indicates excess of chlorine. If care is not taken to touch *fresh portions* of the paper at each trial, a drop may be placed upon a previous one containing excess of arsenite, and the result be misleading. The addition of the arsenite to the chlorine water makes the gradual approach to the end-point easily followed, owing to the decreasing intensity of colour produced.

Exercise 21.—Equation shows that 168 grm. of $NaHCO_3$ produce 106 grm. of Na_2CO_3, consequently about 10 grm. will be necessary to yield 6 grm. (roughly).

Exercise 22.—Since one formula weight of Na_2CO_3 requires two of HCl to neutralize it, evidently 1 l. of N. Na_2CO_3 must contain $\frac{1}{2}$ a formula weight of the salt; i.e. 5.3 grm. in 100 cu. cm.

Exercise 25.—1 l. of $\frac{N.}{10}$ solution should contain 3.647 grm. of HCl, and 250 cu. cm. of approximately $\frac{N.}{10}$ strength, 0.9 grm. HCl.

Exercise 36.—Weight of HNO_3 per litre $= \frac{63.018}{14.01} \times 1.5 = 6.747$ grm. 1 cu. cm. $= 0.00675$ grm. HNO_3.

Exercise 43.—N. Na_2CO_3 contains about 13 grm. of the salt in a $\frac{1}{4}$ l. Take about 5 grm.

Exercise 53.—Equivalent of tartaric acid is 75.

Exercise 54.—Basicity of oxalic acid is 2.

ANSWERS TO QUESTIONS

2. Without the acid a brownish precipitate of hydrated manganous oxide appears, and the liquid becomes alkaline.

$$2\,KMnO_4 + 5\,H_2S = K_2O + 2\,MnO + 5\,S + 5\,H_2O.$$

K_2O and MnO become hydrates. In the presence of H_2SO_4 the reaction proceeds more readily, and soluble metallic sulphates are produced.

$$\begin{aligned}&2\,KMnO_4 + 5\,H_2S + 3\,H_2SO_4\\ &\qquad = K_2SO_4 + 2\,MnSO_4 + 5\,S + 8\,H_2O.\end{aligned}$$

In both cases H_2S is oxidized by the $KMnO_4$ to H_2O and S. The latter may only produce opalescence, or be sufficient to make the liquid appear milky.

4. Add excess of SO_2. This state is indicated by the persistence of its odour. Now boil till all excess has been expelled. The original solution of $K_2Cr_2O_7$ should have an acid reaction and a reddish-yellow colour. The completely reduced product $Cr_2(SO_4)_3$ should be bluish-green.

$$\begin{aligned}&K_2Cr_2O_7 + 3\,SO_2 + H_2SO_4\\ &\qquad = K_2SO_4 + Cr_2(SO_4)_3 + H_2O.\end{aligned}$$

The addition of H_2SO_4 is not so necessary in this reaction, since the H_2SO_3 formed is easily oxidized by the air to H_2SO_4.

5. Silver chromate: Ag_2CrO_4. This decomposes in the presence of NaCl to form AgCl and Na_2CrO_4.

6. Silver chloride is first formed. Silver chromate does

not form permanently till all chloride is precipitated. The first trace of *permanent* red precipitate marks the end-point of the reaction between $AgNO_3$ and NaCl.

7. The colour of neutral solution of methyl orange is buff. Alkalis turn it yellow and mineral acids pink. Its indications with organic acids are not reliable. It is not affected by CO_2 in the solution; hence the gas need not be boiled off when this indicator is used.

8. Phenolphthalein is colourless in neutral and acid solutions, but instantly turns pink in the presence of alkali. The colour disappears, however, on standing. Sutton suggests that this may be due to the hydrolytic action of water as well as to absorption of CO_2 from the air. Phenolphthalein may be used to discover when normal alkali carbonate is just converted into bicarbonate; for the pink colour remains as long as a trace of the normal salt is present.

9. Saliva usually shows neutral reaction with litmus and acid with turmeric.

10. The presence of slight excess of $K_2Cr_2O_7$ cannot be detected, as its colour is obscured by the green chromic compound.

11. "Turnbull's blue." [See note on $K_3FeC_6N_6$, p. 144.]

12. Yellowish-green colour shows excess of $K_2Cr_2O_7$. The blue colour gradually lessens as the end-point is approached.

15. 35.5; 49; 56; 37.

17. 63; 126; 126; 63.

21. (*a*) 0.1295 grm. HCl.
(*b*) 0.6958 ,, H_2SO_4.
(*c*) 0.0425 ,, NH_3.
(*d*) 0.0074 ,, $Ca(OH)_2$.
(*e*) 0.4876 ,, Na_2CO_3.

22. 15.33 grm.; 20.15 l.

23. An equal number.

24. The alkali. Alkali : acid = 26.4 : 25.

25. A's acid : B's acid = 17.5 : 15.

26. Neutralizing power of HCl : that of H_2SO_4 = volume of H_2SO_4 used : volume of HCl.

27. N. HCl contains a mol (or gramme molecular weight) of the acid per litre; or 18.234 grm. per half-litre. In the example given, it is supposed that 1 cu. cm. of the bench acid = 0.086 grm. HCl; therefore the number of cubic centimetres of this acid containing 18.234 grm. HCl is $\frac{18.234}{0.086}$, or 212 cu. cm.

29. (*a*) 0.3811 grm. HCl.
   (*b*) 1 cu. cm. = $\frac{23}{53} \times 0.06 = 0.026$ grm. Na.
   (*c*) 1 cu. cm. = 0.052152 grm. Na_2CO_3.

30. $25 \times \frac{1}{0.975} = 25.6$ cu. cm.

32. (*b*) $$\frac{\text{No. of molecules } H_2SO_4}{\text{No. of molecules } H_2O} = \frac{\dfrac{\text{percentage of } H_2SO_4}{\text{formula weight of } H_2SO_4}}{\dfrac{\text{percentage of } H_2O}{\text{molecular weight of } H_2O}}.$$

91.5 per cent of H_2SO_4 to 8.5 per cent of H_2O agrees with H_2SO_4, 2 H_2O.

33. (*a*) N. × 2.5.
   (*b*) $\frac{N.}{10}$ HNO_3; or 1 cu. cm. = 0.006302 grm. HNO_3.
   (*c*) To $\frac{1}{5}$ its strength. Say 50 cu. cm. to 250 cu. cm.

36. The tubes usually contain lime or soda-lime. Their use is to prevent access of CO_2 to the alkali, and the consequent production of carbonate which might lead to error. The alkali attacks glass, and tends to fix glass taps and stoppers.

39. The strength will be found to be under 0.002 grm. per cubic centimetre. N. $Ca(OH)_2$ should contain 0.037043 grm. per cubic centimetre. The answer should be near $\frac{N.}{20}$.

40. The end-point could not be distinguished. By adding Na_2CO_3 till a bluish tint appears, not only the $\frac{N.}{10}$ acid but the H_2CO_3 set free will have been neutralized; and driving off any CO_2 by boiling will then only intensify, if possible, the blue colour.

43. (*a*) $\frac{18.5}{18.75} \times 100 = 98\frac{2}{3}$ per cent Na_2CO_3.

(*b*) $2.65 \times \frac{100}{98\frac{2}{3}} = 2.686$ grm.

44. The Ca is present as bicarbonate $CaH_2(CO_3)_2$, which breaks up on boiling when $CaCO_3$ is precipitated, owing to escape of CO_2. The dissolved $CaSO_4$ reacts with Na_2CO_3 to form $CaCO_3$, which is precipitated, whilst Na_2SO_4 remains dissolved.

45. (*a*) 0.68 grm. (*b*) 10 litres.

49. (*a*) Since $\frac{\text{weight of NaOH}}{\text{weight of } H_4C_2O_2} = \frac{2}{3} = \frac{40}{60}$, 60 grm. of acid should be present to the litre.

(*b*) This weight includes 4 grm. of hydrogen, 1 grm. only of which is displaced by 23 grm. of Na. Therefore one hydrogen atom only appears to be responsible for the acidity, and the acid is monobasic.

50. Since the acid is dibasic, its gramme formula weight is the number of grammes in that volume of the acid $= 171.4$ grm. $Ba(OH)_2$.

51. Acid : alkali = 3 : 2.

52. Acid : alkali = 39 : 20.

53. Let x = number of atoms of Ba in 50 cu. cm. Since 1 atom of Ba = 2 atoms of K, there are $2x$ atoms of K in 40 cu. cm., and $2x \times \frac{50}{40}$ in 50 cu. cm. ∴ in equal volumes

$$\frac{\text{Number of atoms of Ba}}{\text{Number of atoms of K}} = \frac{x}{2x \times \frac{50}{40}} = \frac{2}{5}.$$

54. 55.84 grm. Fe.: practically $\frac{1}{7}$ of the formula weight.

55. ~~5.3~~ grm. oxalic crystals.

6,303

56. For 0.549 grm. Mn, there should be 1.58 grm. $KMnO_4$, since the formula weight contains 54.9 parts Mn. Since N. $KMnO_4$ contains 31.6 grm. of the salt per litre, the solution is $\frac{N.}{20}$.

(*a*) The iron solution is $\frac{245}{25} \times \frac{N.}{20}$; a litre contains $2.79 \times \frac{245}{250}$, or 3.418 grm. Fe″.

(*b*) 1 cu. cm. = 0.00158 grm. $KMnO_4$; 0.0004 grm. oxygen; and 0.00279 grm. Fe″.

57. Half a gramme formula weight of oxalic acid crystals.

59. (*a*) 1 cu. cm. = 0.001416 gramme $KMnO_4$.
(*b*) 750 cu. cm. contain 1.062 grm. $KMnO_4$; ∴ 78 cu. cm. water must be withdrawn to make the solution $\frac{N.}{10}$.

60. H_2O_2 breaks up thus: $2\,H_2O_2 = 2\,H_2O + O_2$, so that 40 grm. of peroxide yield 18.8 grm. oxygen.

61. (*a*) 944.5 cu. cm. $\frac{N.}{8}$ $KMnO_4$.
(*b*) 1.3 l.

62. 49 grm.

64. 1.55 grm. $K_2Cr_2O_7$.

65. The $KMnO_4$ solution is $\frac{25}{17.5} \times \frac{N.}{10}$. Therefore a litre will yield $0.8 \times \frac{25}{17.5}$, or $1\frac{1}{7}$ grm. oxygen. The $K_2Cr_2O_7$ solution is $\frac{25}{28.2} \times \frac{N.}{10}$; and a litre will yield $1\frac{9}{91}$ grm. oxygen.

66. $4\frac{1}{6}$ grm. CrO_3 per litre. The equation

$$6\,FeSO_4 + 2\,CrO_3 + 6\,H_2SO_4 = 3\,Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + 6\,H_2O$$

shows that 151.9 grm. $FeSO_4$, or 55.8 grm. Fe″, reduce 200 grm. of CrO_3. Also $2\,CrO_3 = Cr_2O_3 + 3\,O$; i.e.

200 grm. of CrO_3 yield 48 grm. of oxygen; 0.8 grm. oxygen will thus be got from $\frac{200}{60}$ grm. CrO_3. But the solution is evidently $\frac{N.}{10} \times \frac{5}{4}$; therefore the solution contains $\frac{200}{60} \times \frac{5}{4}$ grm., or $4\frac{1}{6}$ grm. per litre.

67. See table of standard solutions in common use, p. 145.

68. Make up some $\frac{N.}{10}$ $K_2Cr_2O_7$. Titrate the ferrous solution against this, and also against the permanganate. Suppose it is found that 25 cu. cm. of Fe″ solution = 26.5 cu. cm. $K_2Cr_2O_7$ solution and 21.2 cu. cm. $KMnO_4$ solution; the strength of the ferrous solution is $\frac{N.}{10} \times \frac{26.5}{25}$; and the strength of the permanganate solution $\frac{N.}{10} \times \frac{26.5}{25} \times \frac{25}{21.2}$ or $\frac{N.}{10} \times \frac{26.5}{21.2}$. A litre of the permanganate solution contains $3.16 \times \frac{26.5}{21.2}$ grm. $KMnO_4$.

69. First reduce to arsenite with SO_2 as follows:—Place about 0.5 grm. of the arsenate and some 40 cu. cm. saturated solution of the gas in a stoppered bottle; tie down the stopper, and digest in boiling water for one hour. Allow to cool before the stopper is removed. To get rid of excess of SO_2 add twice the volume of water to the solution, and boil down to half. Cool again, then make up to a definite volume with freshly distilled water (M‘Kay). Estimate the arsenite as given in Exercise 75.

70. Equal volumes should be used. $K_2Cr_2O_7$ oxidizes KI, and its oxidizing value is given by the weight of iodine liberated. The relationship between the weights of iodine and $Na_2S_2O_3$ has been given previously.

74. 80 per cent MnO_2.

75. Sufficient $K_2Cr_2O_7$ must be added to precipitate all barium before Ag_2CrO_4 can be formed.

78. 1 grm. NaCl would require 2.9 grm. $AgNO_3$
1 ,, NaBr ,, 1.65 ,, ,,

$$\frac{\text{weight of NaCl}}{\text{weight of NaBr}} = \frac{2 - 1.65}{2.9 - 2} = \frac{0.35}{0.9}.$$

28 per cent NaCl; 72 per cent NaBr.

79. Since NH_3 does not interfere with precipitation of AgI, add a few drops of KI to act as indicator. The appearance of a trace of this yellow precipitate marks the end-point.

INDEX

A

Acetic acid, 71.
Acidimetry and alkalimetry, 35.
— organic acids, 67.
Acidity, cause of, 26, 27, 136.
— of vinegar, estimation of, 67.
Acids (organic), basicity and molecular weight, 69.
Alkalinity, cause of, 136.
Alloy of silver and copper, estimation of, 116.
Alum, indicator, 116.
Ammonia, solution of, its estimation, 49, 66.
Ammonium bisulphite as reduction agent, 88.
— salts, estimation of, 62.
— thiocyanate, use of, 114.
Anions, 135.
Answers to questions, 153.
Antimony, estimation of, 95.
Apparatus for measuring liquids, 5.
Arsenate, estimation of, 158.
Arsenious oxide, decinormal solution of, 94.
— — estimation of, 94.
Atomic weights, table of, 150.
Available chlorine, estimation of, 100, 103, 128.
— oxygen, estimation of, 86, 101, 102.

B

Backward titration, 54, 98.
Barium compounds, estimation of, 55, 68, 128.
Basicity of organic acids, 69, 70.
Bleaching powder, estimation of, 100, 103, 128.
Bone ash, estimation of, 124.
Borax, estimation of, 125, 126.
— ionization of, 137.
Boron trioxide, estimation of, 126.
Brass, estimation of copper and zinc in, 119, 121.
Bromine water, estimation of, 99.
Bunsen's distillation method, 105.
Burettes, 7, 12.

C

Calcite, estimation of, 126.
— used to standardize hydrochloric acid, 56.
Calcium compounds, determination of solubility, 49, 57.
— phosphate, standard solution of, 124.
Calculation of results, 40, 52, 56, 63.
Calibration of flasks, 9.
Carbon dioxide in soda water, estimation of, 62.
Carbonates, litmus used to estimate, 50.
Carnegie's method, 83.
Caustic soda, estimation of, 47, 52, 66, 127.
Chlorides, estimation of, 110, 112.
Chlorine available in bleaching powder, estimation of, 100, 103, 128.
— liberated by manganese dioxide, estimation of, 105.
— water, estimation of, 99.
Choice of indicators in acidimetry and alkalimetry, 35.
Chromium trioxide, estimation of, 106.
Completion of a reaction, how to determine, 14.
Conditions necessary for accurate estimations, 3.
Copper, estimation of, 102, 120, 121.
Cyanides, estimation of, 113.
Cylinders, measuring, 6, 13.

D

Decinormal solutions, 26, 145.
Degrees of hardness of water, estimation of, 60, 61.
Detection of end-point, 14.
Dilution of solutions to standard strength, 41, 43, 77.
— (rough) of strong solutions, 39.
Direct method in acidimetry and alkalimetry, 36.
— — of estimating ammonia, 64.
— — of oxidation and reduction, 72.
Dissociation, 134, 140.
Drop reagents, 22.
Drying the inside of a flask, 10.

E

Electrolytes and electrolytic dissociation, 134.
Empirical solutions, 145.
End-point, 2, 15.
Equivalent, 67, 70.
— determination of, 69, 129, 130.
Estimation of acetic acid, 67.
— — acids and alkalis, 35, 56, 67.

Estimation of acidity of vinegar, 67.
— — alkalis, 47, 49, 50, 51, 52, 58, 66, 127.
— — ammonia (free), 49, 66.
— — ammonium compounds, 62, 64, 66.
— — antimony, 95.
— — arsenate, 95, 158.
— — arsenious oxide, 94.
— — barium compounds, 55, 68, 128.
— — bleaching powder, 100, 103, 128.
— — bone ash, 125.
— — borax, 125, 126.
— — bromide, 113.
— — bromine water, 99.
— — calcium compounds, 49, 57, 100, 103, 110, 125, 128.
— — carbon dioxide in soda water, 62.
— — carbonates, 50, 51, 58, 126.
— — caustic alkali, 47, 52, 58, 66, 127.
— — chloride, 66, 110, 112, 127.
— — chlorine available, 100, 103, 128.
— — — water, 99.
— — chromate, 106.
— — copper, 102, 120, 121.
— — cyanides, 113, 114.
— — dichromate, 87, 106.
— — halides, 107.
— — hardness of water, 60, 61.
— — hydrochloric acid, 39, 43, 48, 56, 128.
— — hydrogen peroxide, 85, 102.
— — hypochlorite, 100, 103, 129.
— — iodine solution, 92.
— — iron, 81, 83, 87, 88, 133, 134.
— — lead, 129.
— — lead dioxide, 104.
— — manganese dioxide, 105.
— — mercury, 130.
— — mixtures: acids, 128, 130.
— — — acid and salt, 130.
— — — alkali and salt, 58, 127.
— — — ammonia and caustic soda, 66.
— — — carbonate and chloride, 127.
— — — carbonate and sulphate, 53.
— — — chlorides, 66, 110, 112.
— — — chloride and hydrochloric acid, 127.
— — — chloride and sulphate, 54.
— — — metals, 116, 119, 121.
— — — nitric acid and silver nitrate, 109.
— — — oxalic acid and a salt, 84, 127, 130, 131.
— — nitrite, 131.
— — organic acids, 67, 79, 126, 129.
— — permanganate, 76, 77, 79, 101, 127.
— — phosphates, 121, 124.
— — potassium dichromate, 87.
— — silver, 110, 116.
— — soda ash, 58.
— — sulphate, 46, 54.
— — sulphite, 97.
— — sulphur dioxide solution, 96, 98.
— — tartar emetic, 95.
— — thiosulphate, 98.
— — tin, 132.
— — water molecules (combined), 46, 53, 81.
— — zinc, 119, 132, 133.
Estimations, backward titration methods, 54.
— conditions necessary for, 3.
Estimations, direct methods, 36.
— indirect oxidation methods, 90.
— oxidation methods, 72.
— precipitation methods, 107.
Etching flasks, 10.
Exercises, notes on, 151.
External indicators, 22.

F

Factors, 33, 44, 87.
Faraday, 134.
Ferric compound reduced to ferrous, 82, 83.
— condition, to prevent, 77, 78.
Ferrous ammonium sulphate, to prepare, 75.
— sulphate, 77.
Ferrum redactum, 133.
Flasks, to calibrate, dry, and etch, 9, 10.
Floats, 8, 12.
Friend, Dr., 75.

G

Gasometric method, 133, 134.
Gay-Lussac's method, 110.
Graduated vessels, 6, 7, 10.
Gramme equivalent, 28.
Gravimetric methods, 1, 46, 57, 68.

H

Halogens as oxidizing agents, 90.
Hantzsch, 139.
Hardness of water, to estimate, 60, 61.
Hehner's method, 60.
Heights of liquids, to read, 13.
Hydrion, 136.
Hydrochloric acid, to estimate, 39, 43, 48, 56.
— — (standard), to prepare, 41.
Hydrogen peroxide, to estimate, 85, 102.
Hydroxidion, 136.
Hypochlorites, 99, 100, 103, 128, 129.

I

Indicators, 3, 15, 18, 22, 93, 109, 115, 116, 118, 123, 134.
— choice of, in acidimetry, &c., 35.
— theory of, 137.
— two used in one estimation, 58.
Indirect methods, 62, 90.
Iodide of starch, 143.
Iodine, 22, 23, 92.
— standard solution of, 91.
— to purify, 91.
Iodized starch paper, 23, 143.
Iodometry, 96.
Ions, 134, 136.
Iron, to estimate, 81, 83, 87, 88, 133, 134.

K

Kations, 135.
Kingzett's method, 102.
"Known strength", 2, 3.

L

Lead, alkaline solution of, 118.
— to estimate, 129.
Liebig's method, 113, 114.
Lime water, to estimate, 49.
Litmus, 15, 19, 20, 35, 51, 138, 140.
Löwenthal's method, 132.

M

Manganese dioxide, estimation of, 104, 105.
— sulphate, use of, 75, 133.
Measurement of liquids, apparatus for, 5.
Mercury, estimation of, 130.
Method, Bunsen's, 105.
— Carnegie's, 87.
— direct for estimating ammonia, 64.
— gasometric, 133, 134.
— Gay-Lussac's, 110.
— gravimetric, 1, 46, 57, 68.
— Hehner's, 60.
— indirect, for estimating ammonia, 62.
— Kingzett's, 102.
— Liebig's, 113, 114.
— Löwenthal's, 132.
— M'Kay's, 158.
— Mohr's, 109, 110.
— Moody's, 41.
— oxidation, direct, 72.
— — indirect, 90.
— Parkes', 120.
— Personne's, 130.
— precipitation, 107.
— Rakow's, 110.
— Volhard's, 115, 116.
— Wenig's, 46.
Methyl orange, 20, 35, 141.
Mixtures, estimation of, 53, 54, 66, 81, 84, 109, 110, 112, 113, 114, 116, 127, 128, 130, 131.
— of two salts with one radical in common, 112.
Mohr's burette, 7.
— method, 109, 110.
— salt, preparation of, 75.
Mol, 49.
Molar and molecular solution, 25.
Molecular weight determined, 69, 70.
Molecules of combined water estimated, 46, 53, 81.
Moody's method, 41.

N

N, $\frac{N}{2}$, 2 N, &c., solutions, 26, 145.
Neutralization, 36, 38, 136.
Nitric acid, estimation of, 109.
Nitrite, estimation of, 131.
Normal solutions, 26, 145.
Notes on exercises, 151.

O

Organic acids, estimation of, 67.
— — equivalent of, 67.
— — molecular weight of, 69.
Oxalic acid, 70, 79, 84, 126, 127.
Oxidation methods, 72, 90.
Oxygen available, 86, 101, 102.

P

Parkes' method, 120.
Peroxide of hydrogen, estimation of, 85, 102.
Personne, 131.
Phenolphthalein, 21, 36, 138, 139.
Phosphates, estimation of, 122, 124.
Picric acid, 139.
Pipettes, 7, 11.
Potassium carbonate, estimation of, 51.
— chloride, estimation of, 110.
— chromate, 142.
— cyanide, 120, 121, 122, 137.
— — estimation of, 114, 120.
— dichromate, 22, 30, 86, 87.
— — estimation of, 106.
— ferricyanide, 24, 81, 144.
— ferrocyanide, 123.
— iodide, 98, 99, 102, 103.
— permanganate, 16, 28, 72, 77, 82, 127.
— thiocyanate, 114, 115.
Precipitation methods, 107.
Preparation of iodized starch paper, 23.
— — litmus solution, 19.
— — methyl orange solution, 20.
— — Mohr's salt, 75.
— — oxalic acid, 79.
— — phenolphthalein solution, 21.
— — sodium carbonate (dry), 38.
— — — chloride crystals, 108.
— — standard solutions, 30.
— — — — of arsenious oxide, 94.
— — — — — barium hydroxide, 68.
— — — — — calcium phosphate, 124.
— — — — — caustic soda, 52.
— — — — — copper salt, 121.
— — — — — ferrous sulphate, 77.
— — — — — hydrochloric acid, 41.
— — — — — iodine, 91.
— — — — — microcosmic salt, 123.
— — — — — permanganate, 76.
— — — — — potassium cyanide, 121.
— — — — — — dichromate, 87.
— — — — — silver nitrate, 109.
— — — — — sodium carbonate, 38.
— — — — — — chloride, 108.
— — — — — — sulphide, 117.
— — — — — — thiosulphate, 92.
— — — — — sulphuric acid, 45, 46.
— — — — — tartaric acid, 68.
— — — — — thiocyanate, 115.
— — — — — uranyl acetate, 123.
— — starch solution, 22.
Purification of arsenious oxide, 95.
— — iodine, 91.

Q

Questions, answers to, 153.

R

Rakow's method, 110.
Reading heights of liquids, 13.
Record of work, 37, 40.
Reduced iron, estimation of, 133, 134.
Reducing solution to standard strength, 41, 43, 77.
Reduction by ammonium bisulphite, 86, 88.
— — stannous chloride, 86, 89.
— — zinc, 82, 83, 86.
— factor, 33, 44, 87.
— methods, 72.
Residual methods of analysis, 55.
Results, how to calculate, 40, 52, 56, 63.
— — — tabulate, 40.

S

Salammoniac, estimation of, 62.
Salts, standard solutions of, 28.
Silver, estimation of, 110, 116.
— chromate, 18, 109.
— nitrate, standard solution of, 109.
— — use of, 107.
Soda ash, estimation of, 58.
Soda-water, estimation of carbon dioxide in, 62.
Sodium acetate, 137.
— arsenite, 23, 94.
— bicarbonate, use of in iodometry, 93, 95, 96.
— carbonate, estimation of, 50, 58.
— — (dry), preparation of, 38.
— chloride, estimation of, 66.
— — crystals, preparation of, 108.
— — to prepare standard solution of, 109.
— hydrogen sulphate, estimation of, 54.
— hydroxide, estimation of, 47, 52, 66.
— hypochlorite, estimation of, 129.
— nitrite, estimation of, 131.
— oxide (in carbonate), estimation of, 50.
— phosphate, 137.
— — estimation of, 124.
— sulphide, standard solution of, 116, 117.
— sulphite, estimation of, 97.
— thiosulphate, 92, 97.
— — estimation of, 98.
Solubility of calcium compounds determined, 49, 57.
— — oxalic acid determined, 126.
Solution of known strength, 2, 3.
— — litmus prepared, 19.
— — methyl orange prepared, 20.
— — phenolphthalein prepared, 21.
Solutions, empirical, 145.
— molar, 25.
— molecular, 25.
— normal, 26.
Solutions of "equal strength", 27.
— reduced to standard strength, 43.
— standard, 25, 145.
— — table of, 145.
— to reduce very strong, 39.
— volumetric, 25.
Specific gravity method, 45.
Standard solutions, 25, 145. (Also see Preparation of standard solutions.)
Stannous chloride as reducing agent, 86, 89.
Starch, 22, 142.
— paper (iodized), 23, 143.
Strength of solutions, 3, 4, 25, 145.
"Strong" acids, bases, &c., 67, 135.
Sulphur dioxide, estimation of, 96, 98.
Sulphuric acid, estimation of, 45, 46, &c.
Sutton, 140.

T

Table of atomic weights, 150.
— — standard solutions, 145.
Tabulating results, 40.
Tartar emetic, estimation of, 95.
Tartaric acid, equivalent determined, 69.
Thiocyanate, use of, 114.
Thiosulphate, use of, with iodine, 97.
Tin, estimation of, 132.
Titration, 33, 36.
— backward method, 54.
Tropæolin D, 141.
Turmeric, 21, 142.

U

Uranyl acetate, 122, 123.

V

Vinegar, its acidity estimated, 67.
Volhard's method, 115, 116.
Volumetric methods, 1, 2.
— solutions, 25, 145.

W

Water combined, estimation of, 46, 53, 81.
— hardness of, estimated, 60, 61.
Weak acids and bases, 67, 135.
Weighing bottle, 50.
Weight of a litre of water, 5.
Wenig's method, 46.
Wollaston, 71.
Work, how to record, 37, 40.

Z

Zinc as reducing agent, 82, 83, 86.
— estimation of, 119, 132, 133.

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